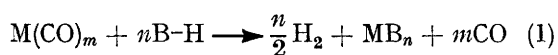


Reactions of Some Metal Carbonyls with Chelating Compounds containing Active Protons, especially Schiff's Bases

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Reactions of several metal carbonyls with chelating ligands containing active protons have been carried out. The reactions of hexacarbonylchromium and hexacarbonylmolybdenum with *N*-methylsalicylideneimine led to the formation of the corresponding *N*-methylsalicylideneiminato-complexes of chromium(III) and molybdenum(III). These are most probably monomeric octahedral complexes as suggested by the magnetic moments which are somewhat lower than the spin-only value, as expected for a d^3 octahedral configuration. Reactions of decacarbonyldimanganese with *NN'*-ethylenebis(salicylideneimine), SaEnH₂, and with *NN'*-trimethylenebis(salicylideneimine) yielded the corresponding manganese(II) complexes; the *NN'*-trimethylenebis(salicylideneiminato)-derivative was found to absorb one mol. of oxygen as previously announced but no confirmation could be found of a similar absorption of molecular nitrogen. Pentacarbonyliron and SaEnH₂ gave the air-sensitive FeSaEn together with some reaction by-products which were not fully identified. FeSaEn is a high-spin compound of d^6 configuration and is converted by molecular oxygen into the μ -oxo-iron(III) derivative. If the *trans*-effect is of some importance in octahedral complexes, it seems that for bivalent metals and with bidentate ligands co-ordination of carbonyl groups to the metal should lead preferentially to *cis*-octahedral structures, whereas with quadridentate planar ligands the co-ordination of two carbonyl groups, necessarily occupying *trans*-positions, is probably not very likely to occur. These ideas have been tested with ruthenium and found to be reasonably well confirmed. Dodecacarbonyltriruthenium and acetylacetone, acacH, give the first example of a bis(acetylacetonato)carbonyl derivative, namely *cis*-Ru(acac)₂(CO)₂. Dodecacarbonyltriruthenium and the Schiff's base *N*-phenylsalicylideneimine, Ph-SaEnH, gave *cis*-Ru(Ph-SaEn)₂(CO)₂, a rather labile complex in polar solvents. Dodecacarbonyltriruthenium and SaEnH₂ gave a very robust compound of probable formula RuSaEn₂CO; a dimeric structure with terdentate oxygens has been suggested for this complex. Octacarbonyldicobalt and SaEnH₂ gave CoSaEn in dimethylformamide. Octacarbonyldicobalt and *NN'*-ethylenebis(acetylacetonimine), acacimH₂, by gentle heating in heptane gave the tetracarbonylcobaltate [Co(acacimH₂)₃][Co(CO)₄]₂. The cobalt(II) derivative Co acacim reacts promptly with nitric oxide to give the nitrosyl derivative Co acacim NO.

SOME reactions of metal carbonyls with organic substances containing acidic hydrogen atoms have been reported in the case of enolisable β -diketones^{1,2} and carboxylic acids.³ These reactions can be formally regarded as electron transfers (1) from the zero-valent metal to the hydroxyl proton of either the enolic form of the β -diketone or the carboxylic acid, in which B is the



conjugated base of the acid, the metal being in the $n+$ oxidation state in the final reaction product.

The reactions of aminotroponeimines with pentacarbonyliron(0) to give the corresponding iron(II) chelates have recently been reported.⁴

Metal carbonyl derivatives can also interact with chelating compounds containing active protons without change of the oxidation state of the metal involved. This is the case, for example, of the reaction of bis[dicarbonyl- μ -chloro-rhodium(I)] with 8-hydroxyquinoline⁵ to give 8-hydroxyquinolinatodicarbonylrhodium(I) which is essentially a ligand exchange reaction.

We now report further extensions of reaction (1) to a number of Schiff's bases. In some cases intermediates have been isolated. We also report the reaction of dodecacarbonyltriruthenium with acetylacetone which leads to the first bisacetylacetonato-carbonyl derivative of a transition metal.

EXPERIMENTAL

All reactions and manipulations aimed at the separation of the compounds were carried out under nitrogen. Solvents were deaerated and dried by standard methods. The products were handled according to their degree of reactivity towards oxygen, as specified in each case.

I.r. spectra were measured with Perkin-Elmer 521 and 337 spectrophotometers equipped with gratings.

N.m.r. spectra were measured with a Varian DP 60 A spectrometer.

Magnetic susceptibility was measured with a Gouy balance at different magnetic fields. In all cases χ is quoted in c.g.s.e.m.u.

Molecular weights were determined on tetrahydrofuran solutions of the compounds with a Mechrolab vapour pressure osmometer model 301 A.

Tris-(*N*-methylsalicylideneiminato)chromium(III).— Hexacarbonylchromium (2.2 g.; 10 mmoles) in toluene (100 ml.) was treated with *N*-methylsalicylideneimine (4.2 g.; 31 mmoles) at reflux temperature for 6.5 hr. During this time the solution gradually became red and then orange and gas was evolved. Hexacarbonylchromium condensed in the condenser was returned to the reaction mixture from time to time. After partial evaporation of the solvent, *n*-heptane was added to complete the precipitation of the solid. The latter was filtered off and dried (2.8 g.; 61.6% yield). The compound was recrystallised from toluene as a microcrystalline ochre powder, stable in air, soluble in acetone, tetrahydrofuran, and aromatic hydrocarbons (Found: C, 63.5; H, 5.4; Cr, 11.3; N, 9.2. C₂₄H₂₄CrN₃O₃ requires C, 63.43; H, 5.32; Cr, 11.44; N, 9.25%, magnetic susceptibility $\chi_M = 5660 \times 10^{-6}$ (including the diamagnetic

* W. R. McClellan and R. E. Benson, *J. Amer. Chem. Soc.*, **1966**, **88**, 5165.

⁵ R. Ugo, G. La Monica, S. Cenini, and F. Bonati, *J. Organometallic Chem.*, **1968**, **11**, 159.

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¹ M. L. Larson and F. W. Moore, *Inorg. Chem.*, **1962**, **1**, 856.

² T. G. Dunne and F. A. Cotton, *Inorg. Chem.*, **1963**, **2**, 263.

³ E. Bannister and G. Wilkinson, *Chem. and Ind.*, **1960**, 319.

correction = -253×10^{-6}) at 295°K, corresponding to a magnetic moment $\mu_{\text{eff}} = 3.66$ B.M.

Tris-(N-methylsalicylideneiminato)molybdenum(III).—Hexacarbonylmolybdenum (5.0 g.; 19 mmoles) was heated with the Schiff's base (50 ml.) at 130–140° for 5.5 hr. No solvent was used. The reaction product was precipitated with heptane, washed with heptane, and then recrystallised from toluene. A second recrystallisation from toluene-tetrahydrofuran gave the analytically pure compound (6.5 g.; 68.9% yield). The red-brown complex is soluble in tetrahydrofuran and slightly soluble in toluene (Found: C, 57.9; H, 4.95; Mo, 18.9; N, 8.6. $\text{C}_{24}\text{H}_{24}\text{MoN}_3\text{O}_3$ requires C, 57.84; H, 4.85; Mo, 19.25; N, 8.43%), magnetic susceptibility $\chi_{\text{M}} = 5835 \times 10^{-6}$ (including the diamagnetic correction -253×10^{-6}) at 295°K, corresponding to a magnetic moment $\mu_{\text{eff}} = 3.71$ B.M. The tube for the measurement was prepared under nitrogen. The molybdenum compound is sensitive to air. Absorption of oxygen was observed in toluene with formation of a violet solution.

The i.r. spectra of the *N*-methylsalicylideneiminato-complexes of chromium and molybdenum were very similar and did not contain any band in the 2000 cm^{-1} region attributable to carbonyl groups.

Reaction of Decacarbonyldimanganese with NN'-ethylenebis(salicylideneimine) and NN'-trimethylenebis(salicylideneimine).—Decacarbonyldimanganese (3.66 g.; 9.4 mmoles) was dissolved in 60 ml. of tetrahydrofuran and the solution was heated at reflux temperature for 1 hr. To this solution 5.1 g. (19 mmoles) of *NN'*-ethylenebis(salicylideneimine) was added and the reflux conditions were maintained for two days while the reaction flask was irradiated externally with a mercury lamp. After cooling the mixture was filtered. An orange solid was obtained which was dried *in vacuo* (2.65 g.; 44% yield). This product analysed correctly for $\text{C}_{16}\text{H}_{14}\text{MnN}_2\text{O}_2$. Other properties corresponded to those of *NN'*-ethylenebis(salicylideneiminato)manganese(II) reported previously,^{6,7} in particular very high sensitivity to oxygen in the presence of organic solvents.

The reaction of $\text{Mn}_2(\text{CO})_{10}$ with *NN'*-trimethylenebis(salicylideneimine) was carried out under similar conditions. The gas evolved during the reaction was found to contain hydrogen by gas-chromatography. The yield of crude product was 54%. It was recrystallised by addition of heptane to a warm solution of the compound (0.74 g.) in pyridine (50 ml.). By heating at 80° for several hours the solid lost the pyridine of recrystallisation and analysed correctly for *NN'*-trimethylenebis(salicylideneiminato)manganese(II) (Found: C, 60.9; H, 4.9; Mn, 16.3; N, 8.6. $\text{C}_{17}\text{H}_{16}\text{MnN}_2\text{O}_2$ requires C, 60.90; H, 4.81; Mn, 16.39; N, 8.36%). The bright yellow solid has substantially the same properties as the ethylenedi-imine derivative reported above.

We could confirm that in benzene suspension at 25° the compound absorbs one mole of oxygen per manganese atom,⁸ as shown by direct gas-volumetric measurement at atmospheric pressure. No nitrogen absorption was observed under similar conditions.

Reaction of Pentacarbonyliron with NN'-Ethylenebis(salicylideneimine).—Freshly distilled pentacarbonyliron (21.6 g.; 0.11 mole) was dissolved in 150 ml. of anhydrous dimethylformamide. *NN'*-Ethylenebis(salicylideneimine) (28.7 g.; 0.11 mole) was added to the resulting solution which was then heated at 110° for about 2.5 hr. At this

point gas evolution became faster and the temperature of the external bath was decreased to 95° and maintained thereafter for about 20 hr. After cooling, filtration, and abundant washing with dimethylformamide and toluene a solution (solution *A*) and *NN'*-ethylenebis(salicylideneiminato)iron(II) as brown red crystals were obtained. The latter (14.7 g.; 41.4% yield) still contained small amounts of dimethylformamide and was therefore heated for 2 hr. at 100° *in vacuo*. The solid was then analysed without further purification (Found: C, 59.5; H, 4.4; Fe, 16.5; N, 8.8. $\text{C}_{16}\text{H}_{14}\text{FeN}_2\text{O}_2$ requires C, 59.66; H, 4.38; Fe, 17.34; N, 8.70%). The compound is not very sensitive to air when dry but it reacts with oxygen in solution (see below). It is very soluble in pyridine, slightly soluble in dimethylformamide, and substantially insoluble in aromatic hydrocarbons. I.r. spectrum (Nujol mull prepared under nitrogen): 1625vs, 1595vs, 1545vs, 1525vs, 1440vs, 1340, 1325, 1280, 1235, 1185s, 1140s, 1125, 1085, 1050, 1025, 975, 970, 950, 905, 870, 860, 795, 770vs, 760vs, 750s, 745s, 680, 645, 635, 610, 580, 555, 535, 515, 480, 465, 450, and 410 cm^{-1} .

Solution *A* was evaporated to dryness at room temperature. The solid residue was dissolved in 80 ml. of toluene and reprecipitated with 400 ml. of heptane. After filtration and drying *in vacuo* 18.7 g. of a brown-violet solid was obtained which was very sensitive to air even in the solid state and had a much higher solubility in organic solvents than *NN'*-ethylenebis(salicylideneiminato)iron(II). In tetrahydrofuran solution the solid had several bands in the region around 1900 cm^{-1} , namely at 2000, 1990, 1930, and 1890 cm^{-1} .

NN'-Ethylenebis(salicylideneiminato)pyridineiron(II).—*NN'*-Ethylenebis(salicylideneiminato)iron(II) (2.0 g.) prepared as previously described was dissolved under nitrogen in 20 ml. of anhydrous pyridine at 40°. After filtration, the compound was precipitated by addition of 150 ml. of heptane. The red brown compound was filtered off and dried *in vacuo* (1.5 g.). The dry compound is relatively stable in air whereas its solutions are very readily oxidised (Found: C, 62.7; H, 4.9; Fe, 14.1. $\text{C}_{21}\text{H}_{19}\text{FeN}_3\text{O}_2$ requires C, 62.86; H, 4.77; Fe, 13.92%), magnetic susceptibility $\chi_{\text{M}} = 10,397 \times 10^{-6}$ (including the diamagnetic correction -225×10^{-6}) at 294°K, corresponding to a magnetic moment $\mu_{\text{eff}} = 4.95$ B.M.

Reaction of NN'-Ethylenebis(salicylideneiminato)iron(II) with Oxygen.—*NN'*-Ethylenebis(salicylideneiminato)iron(II) (0.54 g.; 1.7 mmoles) was suspended under nitrogen in 15 ml. of tetrahydrofuran and then exposed to an atmosphere of dry oxygen. A slow oxidation took place. After two days a crystalline orange solid was collected and dried (0.44 g.; 78.9% yield). The solid is moderately soluble in acetone and dichloromethane (Found: C, 58.3; H, 4.4; Fe, 17.0; N, 8.5. $\text{C}_{32}\text{H}_{28}\text{Fe}_2\text{N}_4\text{O}_6$ requires C, 58.21; H, 4.27; Fe, 16.92; N, 8.49%). The oxidation of the iron complex was faster in pyridine solution. By addition of heptane, μ -oxobis[*NN'*-ethylenebis(salicylideneiminato)iron(III)] was precipitated and was filtered off. The compound which was dried *in vacuo* at room temperature did not retain any pyridine (Found: C, 58.2; H, 4.25; Fe, 17.0; N, 8.4%). I.r. spectrum (Nujol mull): 1630vs, 1600s, 1540s, 1450s, 1340, 1310, 1240, 1215, 1195, 1145, 1130, 1090, 1050, 1030,

⁷ R. W. Asmussen and H. Soling, *Acta Chem. Scand.*, 1957, **11**, 1331.

⁸ G. L. Johnson and W. D. Beveridge, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 323.

⁶ A. Earnshaw, E. A. King, and L. F. Larkworthy, *J. Chem. Soc. (A)*, 1968, 1048.

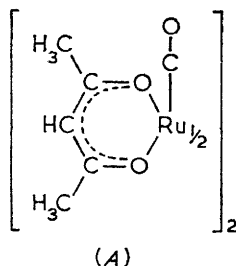
970, 955, 930, 905, 865, 825s, 795, 750s, 745, 735, 650, 635, 625, 610, 595, 540, 510, 470, 455, and 420 cm^{-1} .

In a gas-volumetric experiment carried out in pyridine and dimethylformamide, the absorption of oxygen was found to correspond, within experimental error, to one atom every two iron atoms (*cf.* ref. 8). In a typical experiment in pyridine, 1.39 mmoles of the iron(II) chelate absorbed 0.31 mmole of oxygen at 8° in 27 hr.

Reaction of Pentacarbonyliron with Acetic Acid.—*Preparation of anhydrous bis(acetato)iron(II).* Freshly distilled pentacarbonyliron (29.2 g.; 0.15 mole) was dissolved at room temperature in a solution of 17.9 g. (0.3 mole) of acetic acid and 1.83 g. of acetic anhydride in 100 ml. of dimethylformamide. The mixture was heated to 95°: at this temperature a moderate evolution of gas took place. The temperature was then gradually increased to 115–120° and maintained thereat for 60 hr. The acetate was filtered off, washed with dimethylformamide, and dried *in vacuo* (21 g.; 81% yield). Colourless crystals, practically insoluble in all common organic solvents, moderately stable to moisture. The compound did not show any band around 2000 cm^{-1} attributable to bonded carbon monoxide groups. Absorptions due to co-ordinated acetato-groups were found at 1565 and 1400 cm^{-1} (Found: C, 28.0; H, 3.75; Fe, 31.4. $\text{C}_4\text{H}_6\text{FeO}_4$ requires C, 27.62; H, 3.48; Fe, 32.11%), magnetic susceptibility $\chi_M = 11,380 \times 10^{-6}$ (including the diamagnetic correction = -68×10^{-6}) at 296°K, corresponding to a magnetic moment $\mu_{\text{eff}} = 5.19$ B.M. The magnetic susceptibility was field-independent, thus showing the absence of ferromagnetic impurities.

Preparation of *NN'*-Ethylenebis(salicylideneiminato)iron(II) from Bis(acetato)iron(II).—The iron(II) chelate was also prepared from anhydrous iron(II) acetate and the Schiff's base in dimethylformamide (80.7% yield). The compound was identical (elemental analysis, i.r. spectrum, solubility, and chemical reactivity) with *NN'*-ethylenebis(salicylideneiminato)iron(II) prepared directly from pentacarbonyliron.

Bis(acetylacetonato)dicarbonylruthenium(II) [structure (A)].—Dodecacarbonyltriruthenium (0.26 g.; 0.41 mmole) dis-



solved in 30 ml. of tetrahydrofuran was heated at 150° for 15 hr. with acetylacetone (0.24 g.; 2.4 mmoles) in a stainless-steel autoclave. The mixture was then evaporated to dryness and the solid residue extracted with heptane. By evaporation of the heptane solution, 0.2 g. (46.1% yield) of crude product, still containing small amounts of unchanged $\text{Ru}_3(\text{CO})_{12}$, was obtained. The compound was purified by chromatography on silica gel. Finally the solids obtained by evaporation of some of the chromatographic fractions were recrystallised from heptane. Bis(acetylacetonato)dicarbonylruthenium(II) is pale yellow, m.p. 127–128°. It sublimes at 40°/ca. 10^{-3} mm. Hg. Sublimation is also a convenient method of purification from unchanged $\text{Ru}_3(\text{CO})_{12}$ which is usually the main contaminant. The compound is moderately soluble in tetrahydrofuran

(about 10^{-2}M solutions can be obtained at room temperature) and in hydrocarbons. The i.r. carbonyl stretching vibrations and the proton n.m.r. data are in Table 1. Other i.r. bands were found at 1593m-sh, 1579s, 1539w, and 1523vs cm^{-1} (heptane solution). No band was observed between 1940 and 1600 cm^{-1} (Found: C, 40.7; H, 4.1%; M , 359. $\text{C}_{12}\text{H}_{14}\text{O}_6\text{Ru}$ requires C, 40.57; H, 3.97%; M , 355).

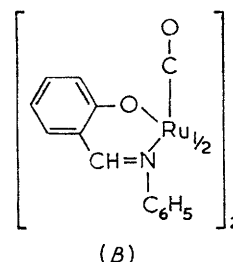
TABLE 1
I.r. and ^1H n.m.r. data for
bis(acetylacetonato)dicarbonylruthenium(II)

ν_{CO} ^a (cm^{-1})	Chem. shift ^b	N.m.r.	
		Multiplicity, integrated area	Assignment
2057s, 2040vw	4.85, ^c 4.82 ^d	Singlet, 2	CH
1988vs, 1959w	8.16, ^c 8.20 ^d	Singlet } 12	CH ₃
	8.32, ^c 8.25 ^d	Singlet }	

^a Heptane solution, 0.1 mm. cell. ^b From tetramethylsilane (τ 10) as internal standard. ^c Deuterioacetone solution. The CH and CH₃ protons of acetylacetone (enol form) in the same solvent are at τ 4.42 and 8.01, respectively. ^d Deuterio-benzene solution.

Bis(acetylacetonato)dicarbonylruthenium(II), identified by its i.r. spectrum and elemental analysis, was also obtained by the following procedure. Tris(acetylacetonato)ruthenium(III) (1.18 g.; 2.96 mmoles) was treated in 50 ml. of tetrahydrofuran with hydrogen (70 atm.) and carbon monoxide (110 atm.) at 160° for 12 hr. The volatile products were distilled off at room temperature *in vacuo* and trapped at -78° ; the i.r. spectrum showed the presence of pentacarbonylruthenium and acetylacetone. The distilled solution was then heated at 150° for 15 hr. in a stainless-steel autoclave. After cooling, the solvent was distilled off *in vacuo* and the solid residue after repeated crystallisations and sublimations finally gave 0.093 g. (8.8% yield) of the desired product.

Bis(*N*-phenylsalicylideneiminato)dicarbonylruthenium(II) [structure (B)].—Dodecacarbonyltriruthenium (0.27 g.; 0.4 mmole) in tetrahydrofuran (35 ml.) was treated with the



Schiff's base (0.50 g.; 2.5 mmoles) in a stainless-steel autoclave at 140° for 15 hr. The most intense i.r. carbonyl bands in the resulting deep red solution were those of the trimeric carbonyl and of the reaction product. The solution was evaporated to dryness and the solid residue was extracted with heptane (45 ml.). The heptane solution was evaporated to dryness and the resulting solid dissolved in heptane-tetrahydrofuran (10:1) and chromatographed on silica gel. The starting ruthenium carbonyl was eluted first followed by the unchanged Schiff's base. The amount of tetrahydrofuran in the eluant was then increased (heptane: tetrahydrofuran = 4:1) and the eluted fractions were controlled by i.r. spectroscopy. The first fraction had

only two intense bands in the carbonyl region. After partial evaporation of the solvent the compound crystallised as yellow needles which were decanted, washed with heptane, and dried *in vacuo* (yield about 1%). The compound is very soluble in tetrahydrofuran, slightly soluble in hydrocarbons. Especially in polar solvents, the initially yellow-orange solution became readily red and the change of colour was accompanied by the appearance of new i.r. carbonyl bands (Found: C, 61.4; H, 3.8; N, 5.21. $C_{23}H_{20}N_2O_4Ru$ requires C, 61.20; H, 3.67; N, 5.10%). I.r. and n.m.r. data are in Table 2.

TABLE 2
I.r. and 1H n.m.r. data for
bis-(*N*-phenylsalicylideneiminato)dicarbonylruthenium(II)

ν_{CO} ^a (cm. ⁻¹)	N.m.r. ^b		
	Chem. shift ^c	Multiplicity, integrated area	Assignment
2046	1.72	Singlet, 1	-CH=N-
1979, 1949vw	2.38—3.50	Complex pattern, 9	Phenyl protons

^a Heptane solution, 1 mm. cell. ^b Deuterioacetone solution. The Schiff's base itself absorbs at τ 1.21 and 2.40—3.25, respectively (deuterioacetone *ca.* 4% solution). ^c From tetramethylsilane (τ 10) as internal standard.

Reaction of Dodecacarbonyltriruthenium with *NN'*-Ethylenebis(salicylideneimine).—Dodecacarbonyltriruthenium (0.47 g.; 0.74 mmole) in 50 ml. of dimethylformamide was heated together with 0.59 g. (2.20 mmoles) of *NN'*-ethylenebis(salicylideneimine), $SaEnH_2$, at 90° for 20 hr. After cooling, the solvent was evaporated *in vacuo*; this left an oily residue which was redissolved in tetrahydrofuran (15 ml.). Heptane (4 ml.) was added until formation of an incipient turbidity and the resulting mixture was allowed to crystallise (about 3 days) at room temperature. The yellow microcrystalline precipitate was decanted, washed with tetrahydrofuran, and dried *in vacuo* (45% yield). The product is stable in air in the solid state and very slightly soluble in polar solvents [Found: C, 50.8, 50.9; H, 3.5, 3.4; N, 6.45, 6.75. ($RuSaEn(CO)_2$), $C_{17}H_{14}N_2O_3Ru$, requires C, 51.64; H, 3.57; N, 7.08. $RuSaEn(CO)_2$, $C_{18}H_{14}N_2O_4Ru$, requires C, 51.06; H, 3.33; N, 6.62%). The i.r. spectrum (Nujol mull) has bands at 1912vs and 1865vw cm^{-1} (probably ^{13}CO). Other bands are at 1645m, 1629s, 1600s, 1556m-w, 1529s, and 1448vs cm^{-1} .

Reaction of Octacarbonyldicobalt with *NN'*-Ethylenebis(salicylideneimine).—Octacarbonyldicobalt (3.75 g.; 11.0 mmoles) was introduced into 100 ml. of dimethylformamide at room temperature. Carbon monoxide was evolved owing to reaction ⁹ (2). The resulting pink solution



was filtered into a dimethylformamide solution (100 ml.) containing 42.5 mmoles of *NN'*-ethylenebis(salicylideneimine). After heating at 120—130° for 8 hr., the red-brown solution was cooled to room temperature and the deep brown crystals of *NN'*-ethylenebis(salicylideneiminato)cobalt(II)

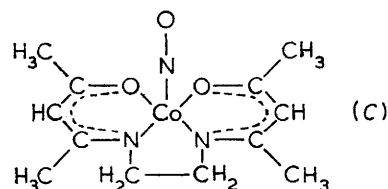
were filtered off, washed with toluene, and dried *in vacuo* (3.03 g.; 42.5% yield). The compound was analytically and spectroscopically identical with an authentic sample of *NN'*-ethylenebis(salicylideneiminato)cobalt(II).

Reaction of Octacarbonyldicobalt with *NN'*-Ethylenebis(acetylacetoneimine).—(a) *In heptane.* Octacarbonyldicobalt (1.50 g.; 4.39 mmoles) was added at 50° to a solution of the Schiff's base (0.98 g.; 4.37 mmoles) in 75 ml. of heptane. Gas evolution soon began and a pink solid precipitated. After 4 hr. the mixture was cooled to room temperature and filtered. The weight of the precipitate after washing with heptane and drying corresponded to a substantially quantitative yield based on the Schiff's base used. The filtrate was found to contain unchanged $Co_2(CO)_8$. The analytical data of the pink precipitate were in agreement with its formulation as the tetracarbonylcobaltate $[Co(Schiff\ base)_3][Co(CO)_4]_2$ (Found: C, 49.6; H, 5.6; Co, 16.3; CO, 22.05; N, 7.9. $C_{44}H_{40}Co_3N_6O_{14}$ requires C, 49.22; H, 5.63; Co, 16.46; CO, 20.87; N, 7.83%). The tetracarbonylcobaltate was sensitive to air in the solid state; its i.r. spectrum as a Nujol mull had bands at 1885 and 550 cm^{-1} , assigned to the C—O and Co—C stretching vibrations of the $[Co(CO)_4]^-$ anion of symmetry $T_d^{10,11}$ respectively.

(b) *In tetrahydrofuran.* The reaction of octacarbonyldicobalt with the Schiff's base in this solvent did not lead to the pure cobalt(II) chelate. Even after prolonged heating at reflux temperature products showing i.r. bands at 1888 and 550 cm^{-1} due to the tetracarbonylcobaltate anion were obtained. The nature of this impurity, certainly different from the tetracarbonylcobaltate described above, was not established.

NN'-Ethylenebis(acetylacetoneiminato)cobalt(II) was prepared by a slight modification of the known procedure ¹² from anhydrous cobalt chloride and the Schiff's base in toluene in the presence of ammonia under exclusion of air. The crude product (81% yield) was recrystallised from methanol-water and finally dried *in vacuo* over P_2O_5 .

Reaction of *NN'*-Ethylenebis(acetylacetoneiminato)cobalt(II) with Nitrogen Oxide.—The cobalt(II)—Schiff's base complex (0.27 g.; 0.95 mmole) in 20 ml. of tetrahydrofuran was exposed to an atmosphere of prepurified nitric oxide for 30 min. at 20°. The initially orange solution became deep red. By addition of heptane the nitrosyl complex [structure (C)]



was precipitated; it was then filtered off, dried (0.22 g.; 74% yield), and recrystallised from heptane as black crystals, stable in air, soluble in the common organic solvents, with analysis corresponding to that of the 1:1 nitric oxide adduct (Found: C, 46.45; H, 5.9; Co, 18.85; N, 13.5%; *M*, 303. $C_{12}H_{18}CoN_3O_3$ requires C, 46.31; H, 5.83; Co, 18.94; N, 13.50%; *M*, 311). The comparison of the i.r.

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¹⁰ R. A. Friedel, I. Wender, S. L. Shufler, and H. W. Sternberg, *J. Amer. Chem. Soc.*, 1955, **77**, 3951.

¹¹ K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' J. Wiley, New York, 1963, p. 177; W. F. Edgell, J. Huff, J. Thomas, H. Lehman, C. Angell, and G. Asato, *J. Amer. Chem. Soc.*, 1960, **82**, 1254.

¹² G. T. Morgan and J. D. Main Smith, *J. Chem. Soc.*, 1925, 2030.

spectrum of the nitrogen oxide adduct with that of the starting cobalt(II) chelate revealed the presence of a new intense absorption at 1650 cm^{-1} (Nujol mull) due to co-ordinated nitrogen oxide. The n.m.r. spectrum of this complex is in Table 3.

TABLE 3

^1H N.m.r. data ^a for compound (C)		
Chemical shift ^b	Integrated area	Assignment
5.13	1	CH
6.55	2	CH_2
7.81	3	CH_3
8.00	3	CH_3

^a In CDCl_3 solution. ^b From tetramethylsilane (τ 10) as internal standard. All the peaks are singlets. The peak at τ 6.55 is a broad singlet.

Reaction of NN' -Ethylenebis(salicylideneimine) with Tetracarbonylnickel.—Tetracarbonylnickel (13.5 g.; 0.08 mole) dissolved in tetrahydrofuran was treated with the Schiff's base at 40° for 14 hr. The mixture, containing some solid decomposition products, was filtered and the solid residue recrystallised from chloroform to give the chloroform adduct of NN' -ethylenebis(salicylideneiminato)nickel(II) (43.4% yield) (Found: C, 46.9; H, 3.9; Cl, 24.3; N, 6.9; Ni, 12.7. $\text{C}_{17}\text{H}_{15}\text{Cl}_2\text{N}_2\text{NiO}_2$ requires C, 45.95; H, 3.40; Cl, 23.93; N, 6.30; Ni, 13.21%).

DISCUSSION

Group VI Metals.—The reactions of hexacarbonylchromium and hexacarbonylmolybdenum with N -methylsalicylideneimine led to the isolation of the Schiff's base complexes of chromium(III) and molybdenum(III). During the preparation of this paper O'Connor and West¹³ described some N -substituted salicylideneiminato-complexes of chromium(III), but they did not prepare the methyl derivative.

An octahedral structure is assumed for both the chromium and the molybdenum complexes. Although *cis*- and *trans*-isomers are possible, we have no way of telling which isomer we have prepared by the reaction with the hexacarbonyls.

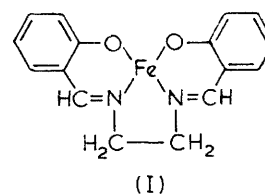
The magnetic moment ($\mu_{\text{eff}} = 3.66\text{ B.M.}$) for the chromium derivative is close to the values found by O'Connor and West¹³ for their N -substituted chromium(III) complexes. A magnetic moment somewhat lower than the spin-only value is usually found for octahedral d^3 configurations.¹⁴

Tris-(N -methylsalicylideneiminato)molybdenum(III) is, to the best of our knowledge, the first tris(salicylideneiminato)-complex of molybdenum reported. Its magnetic moment of 3.71 B.M. at room temperature is somewhat lower than the spin-only value. This is expected¹⁵ for octahedral six-co-ordinate molybdenum(III), thus confirming the structure suggested.

Manganese Complexes.—Decacarbonyldimanganese underwent oxidation by both NN' -ethylenebis(salicylid-

eneimine) and NN' -trimethylenebis(salicylideneimine). All the manipulations for the preparation of the latter compound were carried out under nitrogen, despite which no absorption of molecular nitrogen had occurred, as shown by the elemental analysis. Since also gas-volumetric measurements failed to show any nitrogen absorption, we cannot confirm the previous report by Johnson and Beveridge⁸ concerning the formation of molecular nitrogen adducts with this manganese(II) chelate. On the other hand, we can confirm that NN' -trimethylenebis(salicylideneiminato)manganese(II) absorbs one mole of oxygen, as expected by the same authors.⁸ We do not know, however, whether this oxygen absorption corresponds to a reversible oxygen adduct formation or to an irreversible oxidation of the metal and the ligand. Lewis *et al.* found^{15a} that NN' -ethylenebis(salicylideneiminato)manganese(II) is oxidized by oxygen but the nature of the product was not established conclusively.

Iron Sub-group.—As has been correctly noted by Larkworthy and his co-workers,⁶ considerable confusion existed concerning the magnetic properties of NN' -ethylenebis(salicylideneiminato)iron(II). This was mainly due to the easy oxidation of the iron(II) chelate by air to give the dimeric μ -oxo-iron(III) derivative (see p. 1379). We have prepared the iron(II) chelate, for which the co-ordination around the central metal atom may be assumed to be planar [as indicated in (I)], by the direct



reaction of pentacarbonyliron with the Schiff's base. Incidentally, a dimeric structure for the iron(II) chelate similar to that shown in (III) without the CO groups is not excluded by the available data. In order to establish the identity of the compound, NN' -ethylenebis(salicylideneiminato)iron(II) was also prepared by a straightforward reaction from anhydrous iron(II) acetate and the Schiff's base in dimethylformamide. The two products had identical i.r. spectra. The yields of NN' -ethylenebis(salicylideneiminato)iron(II) from pentacarbonyliron are only moderate because several by-products are also present. These by-products which have not been fully clarified, may conceivably contain carbon monoxide bonded to iron. This is shown by the presence of several i.r. bands in the region around 1900 cm^{-1} , as indicated in the Experimental section. The possibility that some of these bands may be due to salt-like products containing the $[\text{FeH}(\text{CO})_4]^-$ anion or carbonyl anions of higher molecular complexity¹⁶ is

¹³ M. J. O'Connor and B. O. West, *Austral. J. Chem.*, 1968, **21**, 369.

¹⁴ B. N. Figgis and J. Lewis, in 'Modern Co-ordination Chemistry,' ed. J. Lewis and R. G. Wilkins, Interscience, New York, N.Y., 1960, p. 424 *et seq.*

¹⁵ J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 1961, 4590.

^{15a} J. Lewis, F. E. Mabbs, and H. Weigold, *J. Chem. Soc. (A)*, 1968, 1699.

¹⁶ W. Hieber and N. Kahlen, *Chem. Ber.*, 1958, **91**, 2223.

excluded by the very high solubility of these products in toluene (*ca.* 23% w/v). Bands in the same region could be also due to metal-hydrogen stretching vibrations. On the other hand, the presence of iron(III) hydrido-species which could result from hydrogen transfer from the Schiff's base seems unlikely. The low thermal stability of alkyl and aryl derivatives¹⁷ of iron(III) having the *NN'*-ethylenebis(salicylideneiminato) basic structure makes one believe that the analogous hydrido-compound would decompose under the rather drastic reaction conditions. One way of decomposition would be the homolytic fission of the metal-hydrogen bond to molecular hydrogen; hydrogen transfer to the $-\text{CH}=\text{N}-$ bond is also a possibility, however. Copper, nickel, and zinc complexes of *NN'*-ethylenebis(hydroxybenzylamine) have recently been reported.¹⁸ An iron(II) complex of this sort or perhaps better with only one of the two $-\text{CH}=\text{N}-$ groups reduced to $-\text{CH}_2-\text{NH}-$ should show a N-H stretching vibration in the 3200—3500 cm^{-1} region, which was observed. This partial hydrogenation of structure (I) may remove the strain associated with a non-planar configuration of the ligands around the metal, thus favouring also the bonding of carbonyl groups.

The pyridine adduct of *NN'*-ethylenebis(salicylideneiminato)iron(II), FeSaEn,py , has not been reported. Its room temperature magnetic moment of 4.95 B.M. corresponds, within experimental error, to the theoretical spin-only value for a high-spin d^6 system. This result, showing that iron(II) is high-spin in its co-ordination to the quadridentate Schiff's base, is in agreement with previous findings by Calvin and Barkelew¹⁹ and by Larkworthy and his co-workers,⁶ whereas lower values of magnetic moments²⁰ for some ring-substituted derivatives of the same Schiff's base are probably in error. We find that FeSaEn as it is prepared from pentacarbonyliron or from iron(II) acetate is very sensitive to air in solution. We have studied the reaction of FeSaEn with oxygen and found that it occurs according to the stoichiometry (3). Reaction (3) is rather slow



and there was no experimental evidence for the formation of a 1 : 1 adduct with molecular oxygen, although this is probably an intermediate to the formation of the final μ -oxo-species. The latter, which had been previously obtained by Pfeiffer²¹ and Lewis and their co-workers²² was shown²² to contain two spin-free iron(III) centres strongly coupled through the bridging oxygen.

Of particular interest are the i.r. data of $(\text{FeSaEn})_2\text{O}$. Comparison with the spectrum of FeSaEn shows that a new intense band at 825 cm^{-1} is present in the μ -oxo-

derivative. This must therefore be a vibration involving the Fe-O-Fe grouping. Lewis and his co-workers had indicated that complexes containing the metal-oxygen-metal grouping are characterised by i.r. bands between 800 and 1000 cm^{-1} . They were however unable²² to identify that band in the iron(III) μ -oxo-salicylideneiminato-compound because of the multitude of vibrations due to the organic ligand. The 825 cm^{-1} band may be assigned to the asymmetric metal-oxygen stretching vibration. Such a high value for a metal-oxygen stretching vibration is not surprising in view of the partial double-bond character of the metal-oxygen bond^{23,24} in this type of system.

We incidentally found a convenient new way to prepare iron(II) acetate by the direct reaction of pentacarbonyliron with acetic acid in dimethylformamide. This gives, without any further treatment, the anhydrous material. As usually found²⁵ for acetato-compounds of transition metals, the intense asymmetrical and symmetrical C-O stretching vibrations of the acetato-group were observed at 1565 and 1400 cm^{-1} , respectively. The negligible solubility of the compound in the common organic solvents suggests a polymeric structure, probably obtained by acetato-bridges. The magnetic moment at room temperature ($\mu_{\text{eff}} = 5.19$ B.M.) is substantially normal for a high-spin d^6 system, thus suggesting that no important interactions take place between the iron centres in the suggested polymeric structure.

The presence of bands around 1900 cm^{-1} for the by-products of the reaction between pentacarbonyliron and the quadridentate Schiff's base, suggestive of co-ordinated carbon monoxide groups, led us to attempt the reaction of *NN'*-ethylenebis(salicylideneiminato)iron(II) with carbon monoxide. This was unsuccessful even under rather drastic conditions (70°/110 atm.). It is noteworthy that aminotroponeiminato-⁴ and cysteinato-complexes²⁶⁻²⁸ of iron absorb two moles of carbon monoxide under mild conditions. The corresponding dicarbonyl complexes have i.r. bands in the carbonyl stretching region at 2020 and 1972 cm^{-1} (cysteinato-compound,²⁸ KBr pellet) and at 1980 and 1942 cm^{-1} (aminotroponeiminato-compound,⁴ unspecified medium). Both compounds have most probably a *cis*-configuration, as indicated by the presence of two i.r. CO stretching vibrations. The n.m.r. spectra are in agreement with a *cis*-octahedral structure of the dicarbonyl aminotroponeiminato-derivative of iron.⁴ O.r.d. measurements²⁸ for the bis(cysteinato)dicarbonyl derivative of iron have been interpreted to indicate a lack of dissymmetry in the molecule. Since this interpretation may be open to

¹⁷ F. Calderazzo and C. Floriani, *Chem. Comm.*, 1968, 417.

¹⁸ M. J. O'Connor and B. O. West, *Austral. J. Chem.*, 1967, 20, 2077.

¹⁹ M. Calvin and C. H. Barkelew, *J. Amer. Chem. Soc.*, 1946, 68, 2267.

²⁰ S. N. Poddar and K. Dey, *Z. anorg. Chem.*, 1964, 327, 104.

²¹ P. Pfeiffer, E. Breith, E. Lübke, and T. Tsumaki, *Annalen*, 1933, 503, 84.

²² J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc. (A)*, 1967, 1014.

²³ J. D. Dunitz and L. E. Orgel, *J. Chem. Soc.*, 1953, 2594.

²⁴ A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 1961, 396.

²⁵ See ref. 11, p. 197.

²⁶ W. Cremer, *Biochem. Z.*, 1929, 206, 228.

²⁷ M. P. Schubert, *J. Amer. Chem. Soc.*, 1933, 55, 4563.

²⁸ A. Tomita, H. Hirai, and S. Makishima, *Inorg. Chem.*, 1967, 6, 1746.

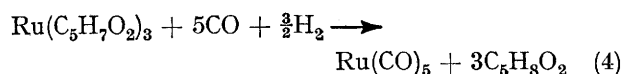
debate in view of possible rapid racemizations, we prefer to regard this compound as having a *cis*-structure too.

The reluctance of carbon monoxide to bond to a metal in the *trans*-position to another carbonyl group is readily understood when considering the known strong *trans*-effect of CO as a ligand, at least in square planar complexes. This may be attributed to the competition by the two carbon monoxide groups for the same *d* orbital of the metal in the formation of the π -back bonding. It can therefore be expected that bonding of carbon monoxide to transition metals in an oxidation state +2 in conjunction with bidentate ligands will occur preferentially to give *cis*-octahedral structures. On the other hand, quadridentate ligands forcing the metal to assume a planar configuration will preferentially tend to induce the co-ordination of only one carbon monoxide group to the metal. Very few examples of transition metals surrounded by a planar quadridentate ligand are known which can form bonds to carbon monoxide: one of these and perhaps the only one existing until now is the (carbon monoxo)haeme-pyridine complex; the CO stretching vibration in this compound has been found²⁹ to be at 1970 cm.⁻¹. It is well known that in the naturally occurring carbon-haemoglobin the axial ligand is an imidazole residue. Strong electron σ -donors such as pyridine and imidazole will act as *trans*-stabilizing groups with respect to the carbon monoxide ligand.

It appeared interesting to test some of these ideas with ruthenium(II) in the hope that the known chemical inertness of its complexes would make the observation of experimental facts easier than with iron(II) in which over-riding kinetic factors may be eventually involved.

Dodecacarbonyltriruthenium was allowed to react with two bidentate ligands, namely acetylacetone and *N*-phenylsalicylideneimine and with a quadridentate ligand, *NN'*-ethylenebis(salicylideneimine) for which a planar arrangement of the donor atoms around the metal seems the most likely.

Bis(acetylacetonato)dicarbonylruthenium(II) was prepared by the reaction of dodecacarbonyltriruthenium with acetylacetone. The preliminary preparation of dodecacarbonyltriruthenium can be avoided by making use of a two-step reaction. In the first step, tris(acetylacetonato)ruthenium(III) was treated with carbon monoxide and hydrogen in tetrahydrofuran. Under the conditions specified in the Experimental section, pentacarbonylruthenium³⁰ is the main product. The stoichiometry can therefore be written as (4). Once

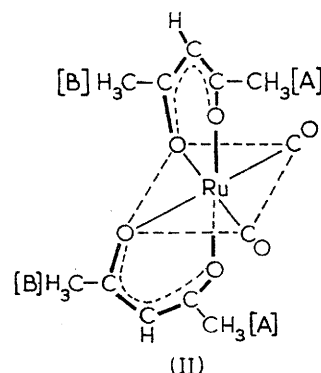


the gas pressure has been released, the next step consists of heating the reaction products in a vessel at

constant volume. The second step can be regarded as an oxidation-reduction of the type represented in equation (1).

Bis(acetylacetonato)dicarbonylruthenium is almost certainly an intermediate of reaction (4) and, for this matter, of the synthesis³¹ of dodecacarbonyltriruthenium from tris(acetylacetonato)ruthenium and CO and H₂ in methanol.

I.r. data suggest that the monomeric bis(acetylacetonato)dicarbonylruthenium(II) has the *cis*-octahedral configuration indicated in (II). Structure (II) of sym-



metry *C*₂ requires two i.r.-active CO stretching vibrations (*A* + *B*): they are observed at 2057 and 1988 cm.⁻¹ in heptane (Table 1). It should be recalled that a *trans* molecule of the same type would have strictly *D*_{2h} symmetry and as such it should give rise to only one stretching vibration (*B*_{1u}). In addition, two much weaker bands are observed at 2040 and 1959 cm.⁻¹. These are most probably the two CO stretching vibrations of the monoisotopically substituted molecule of symmetry *C*₁, Ru(acac)₂(¹³CO)(CO). Additional evidence for the suggested structure comes from the n.m.r. data. These show (Table 1) that the two methyl groups within each ligand are not equivalent, as expected for the arrangement (II). Methyl groups CH₃(*A*) are equivalent and distinct from methyl groups CH₃(*B*). The chemical-shift difference between the two sets of methyl groups is τ 0.16 in deuterioacetone. Similar results have been obtained in the case of *cis*-Ti(Acac)₂X₂, in which X is an alkoxy-group³² or a halogen.³³ The compounds were found to exist in the *cis*-configuration in solution and the two signals of the non-equivalent sets of methyl groups were observed only at low temperature because of a rapid configurational change at room temperature. It is worth mentioning that two distinct methyl resonances were observed for our ruthenium compound, thus indicating that no rapid interchange of methyl sites occurred at room temperature. This is in agreement with the generally observed inertness of ruthenium(II) as compared with the lability of titanium(IV) complexes.³⁴

²⁹ J. H. Wang, A. Nakahara, and E. B. Fleischer, *J. Amer. Chem. Soc.*, 1958, **80**, 1109.

³⁰ F. Calderazzo and F. L'Eplattenier, *Inorg. Chem.*, 1967, **6**, 1220.

³¹ G. Braca, G. Sbrana and P. Pino, *Chimica e Industria*, 1968, **50**, 121.

³² D. C. Bradley and C. E. Holloway, *Chem. Comm.*, 1965, 284.

³³ R. C. Fay and R. N. Lowry, *Inorg. Chem.*, 1967, **6**, 1512.

³⁴ F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Reactions,' J. Wiley, New York, N.Y., 2nd edn., 1967, p. 141 *et seq.*; see also H. Taube, *Chem. Rev.*, 1952, **50**, 69.

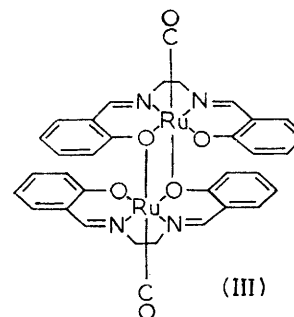
The characteristic i.r. absorption of the co-ordinated acetylacetonato-groups were observed at 1579 and 1523 cm^{-1} . These are well within the range of values found for other acetylacetonato-complexes and following the more recent studies³⁵ on vibrational analysis of bis-(acetylacetonato)copper(II) we assign the observed bands to a predominant symmetrical C-O stretching vibration and an asymmetrical C-C-C stretching vibration, respectively. The absence of i.r. bands between 1600 and 1800 cm^{-1} in the ketonic carbonyl region excludes the possibility that one or both of the acetylacetonato-groups are bonded to the metal through the γ -CH carbon rather than through oxygen as indicated in (II). This mode of co-ordination which has been recently encountered in platinum-acetylacetonato-complexes³⁶⁻³⁸ would leave two free ketonic groups per acetylacetonato-ligand.

Acetylacetonatocarbonyl derivatives of transition metals in an oxidation state +1 have been reported, namely derivatives of rhodium(I),³⁹ manganese(I),⁴⁰ and iridium(I).⁴¹ It is, on the other hand, important to point out that bis(acetylacetonato)dicarbonylruthenium-(II) reported here is the first example of an acetylacetonatocarbonyl of a transition metal in an oxidation state +2. This is even more exceptional when considering that the presence of the electronegative oxygens around the metal appears to make the metal-carbon monoxide bonds rather weak because of the low degree of π -bonding.

Bis-(*N*-phenylsalicylideneiminato)dicarbonylruthenium(II) was obtained from the reaction of dodecacarbonyltriruthenium with *N*-phenylsalicylideneimine. As expected, the presence of the more basic nitrogen donors around the metal strengthens the metal-carbon monoxide bonding. This is suggested by the lower value of the C-O stretching frequencies of bis-(*N*-phenylsalicylideneiminato)dicarbonylruthenium(II) (2046 and 1979 cm^{-1}) than of the corresponding bis(acetylacetonato)-complex at 2057 and 1988 cm^{-1} . The former complex which was isolated in very low yields from the reaction of $\text{Ru}_3(\text{CO})_{12}$ with the Schiff's base is, on the other hand, rather labile as indicated by the change of colour from yellow to red and of the i.r. spectrum upon dissolution in co-ordinating solvents such as tetrahydrofuran and acetone. This solvolytic effect is believed to be responsible for the low yields of isolation of the compound. The presence of two intense and well separated bands in the i.r. C-O stretching region strongly suggests a *cis*-octahedral structure for this Schiff's base dicarbonyl complex.

The reaction of dodecacarbonyltriruthenium with the quadridentate Schiff's base *NN'*-ethylenebis(salicylideneimine), SaEnH_2 , yielded a robust compound analysing correctly for *NN'*-ethylenebis(salicylideneiminato)-

carbonylruthenium(II). Carbon, hydrogen, and nitrogen analyses do not distinguish between a formula with two or one carbon monoxide groups; unfortunately, the compound is stable to pyridine-iodine at about 50°, so that direct carbon monoxide analyses could not be carried out. However, the formulation with one carbon monoxide group per ruthenium is preferred. Only one band is observed at 1912 cm^{-1} . On intensity grounds, this is believed to be a C-O stretching vibration, rather than a metal-hydrogen stretching, being at least twice intense as the C-N stretching vibrations of the organic ligand. A monomeric dicarbonyl compound would have at the most C_{2v} symmetry and, although the C-O stretching vibrations would be allowed by symmetry, one of the two vibrations, the symmetrical one, would presumably be very weak or not observable. Although, therefore, the observation of one C-O stretching vibration does not disprove the dicarbonyl formulation, the insolubility of the compound in the common organic solvents led us to prefer the structure indicated schematically in (III). This is a dimer through oxygen bridges in which one carbonyl group is bonded to hexaco-ordinate ruthenium.



Structures of this type are not unknown. The dimeric *NN'*-ethylenebis(salicylideneiminato)chloroiron(III) has a structure⁴² of the type indicated. The negligible coupling between the CO stretching vibrations of the two units constituting structure (III) may explain the appearance of only one carbonyl band. The rather low value of the CO stretching vibration at 1912 cm^{-1} is suggestive of a rather high metal-carbon bond order. This is in agreement with the chemical inertness of this compound. Unfortunately, the low solubility in the usual organic solvents prevented the measurement of the n.m.r. spectrum of this interesting compound.

In conclusion, it seems that the pattern observed in the reactions of dodecacarbonyltriruthenium corresponds to that expected on the basis of the simple arguments given before. As a matter of fact *cis*-structures have been observed with bidentate ligands and what appears to be a monocarbonyl derivative has been prepared with the quadridentate Schiff's base. Of course, a quadridentate

³⁵ H. Musso and H. Junge, *Tetrahedron Letters*, 1966, 4003.

³⁶ J. Lewis, R. F. Long, and C. Oldham, *J. Chem. Soc.*, 1965, 6740.

³⁷ J. Lewis and C. Oldham, *J. Chem. Soc. (A)*, 1966, 1456.

³⁸ G. T. Behnke and K. Nakamoto, *Inorg. Chem.*, 1968, 7, 330.

³⁹ F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 1964, 3156.

⁴⁰ F. A. Hartman, M. Kilner, and A. Wojcicki, *Inorg. Chem.*, 1967, 6, 34.

⁴¹ F. Bonati and R. Ugo, *J. Organometallic Chem.*, 1968, 11, 341.

⁴² M. Gerloch and F. E. Mabbs, *J. Chem. Soc. (A)*, 1967, 1900.

ligand containing only nitrogen atoms as donors would have been a better test of the suggested pattern. The presence of potentially terdentate oxygen in our Schiff's base may have counteracted the *trans*-co-ordination of a second carbon monoxide group, although we do not believe this to be the case.

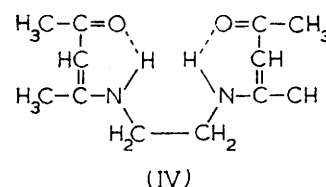
Cobalt and Nickel Complexes.—The reaction of octacarbonyldicobalt with *NN'*-ethylenebis(salicylideneimine) gave Co Salen through the intermediacy of the tetracarbonylcobaltate⁹ arising from the reaction of the carbonyl with dimethylformamide used as solvent. The reaction may be regarded as occurring *via* the displacement of dimethylformamide molecules from $[\text{Co}(\text{DMF})_6]^{2+}$ – $[\text{Co}(\text{CO})_4]_2^-$ by the Schiff's base, followed by H^+ transfer to the $[\text{Co}(\text{CO})_4]^-$ anion. This H^+ transfer would correspond to a reduction, since under the reaction conditions the hydrido $\text{CoH}(\text{CO})_4$ would be rapidly decomposed into H_2 and $\text{Co}_2(\text{CO})_8$. That the final formation of the cobalt(II)–Schiff's base complex occurs by a mechanism similar to that mentioned here is indicated by the fact that in an inert solvent such as heptane the soluble *NN'*-ethylenebis(acetylacetonimine), acacim H_2 , was shown to act as a Lewis base giving the disproportionation reaction to $[\text{Co}(\text{acacimH}_2)_3][\text{Co}(\text{CO})_4]_2$. The latter was identified by elemental analysis and i.r. spectrum.

The reaction of $\text{Co}_2(\text{CO})_8$ with the Schiff's base acacim H_2 in polar solvents in which one would have expected the formation of the chelate *NN'*-ethylenebis(acetylacetoniminato)cobalt(II) led eventually to this product, although contaminated by carbon monoxide-containing compounds. These were not identified. It was thought that one of the contaminating products might have been an adduct of $\text{Co}(\text{acacim})$ with one or two carbon monoxide groups. Reactions were then attempted between Co acacim and carbon monoxide under different conditions. While the runs at room temperature and atmospheric pressure in heptane and tetrahydrofuran were unsuccessful, some reactions under more drastic conditions (140°/150 atm) led to the appearance of carbonyl i.r. bands at about 1900 cm^{-1} , but no pure product could be isolated. The cobalt(II) chelate Co acacim was reported⁴³ to react with oxygen, but the nature of the products was not established and some of the oxygen absorption was irreversible.

On the contrary, *NN'*-ethylenebis(acetylacetoniminato)cobalt(II) reacted smoothly with nitrogen oxide giving rise to the monomeric nitrosyl derivative $\text{Co}(\text{acacim})\text{NO}$. This compound has an i.r. absorption at 1650 cm^{-1} which is characteristic of nitrosyl groups

bonded to transition metals. The compound is probably diamagnetic as suggested by the sharpness of the peaks in the proton n.m.r. spectrum (Table 3). The diamagnetism of the complex suggests that, Co acacim being a d^7 low-spin system and having nitrogen oxide a doublet ground state, pairing of the spins has occurred during complex formation. The nitrogen oxide adduct of *NN'*-ethylenebis(salicylideneiminato)cobalt(II) was also found to be diamagnetic.⁴⁴ The n.m.r. spectrum shows the different positions of the methyl groups which, in each Schiff's base sub-unit, are non-equivalent by symmetry. The suggested structure for this complex is a square pyramid with the basal plane occupied by the Schiff's base and the apical position occupied by the nitrosyl group.

The free Schiff's base in chloroform is to a large extent in the form (IV) as indicated by proton ^1H n.m.r.



measurements:⁴⁵ as far as the methyl and methylene hydrogens are concerned, the comparison of the chemical shifts of the free Schiff's base with those of the nitrosyl complex shows very minor differences. The protons of the CH groups, on the other hand, shift from τ 4.96 in the free Schiff's base (in deuteriated chloroform) to τ 5.13 in the complex. The resonance of the bridging $\text{CH}_2\text{--CH}_2$ group is a broad singlet in the complex. This may be for several reasons, such as the broadening by ^{14}N quadrupole relaxation and intermediate rate equilibria between 'gauche' and 'coplanar' conformations of the methylene groups.

The reaction of salen H_2 with tetracarbonylnickel led, as expected, to the nickel(II) chelate. In this case rather low reaction temperatures are required (about 40°) in agreement with the well known kinetic lability of the carbonyl in substitution reactions. It is believed that the reaction occurs by a preliminary displacement of carbonyl groups by the nitrogen of the Schiff's base and that only in a second step an oxidation–reduction of the type represented in equation (1) takes place.

[8/1543 Received, October 28th, 1968]

⁴⁴ A. Earnshaw, P. C. Hewlett, and L. F. Larkworthy, *J. Chem. Soc.*, 1965, 4718.

⁴⁵ G. O. Dudek and R. H. Holm, *J. Amer. Chem. Soc.*, 1961, 83, 2099.

⁴³ R. H. Bailes and M. Calvin, *J. Amer. Chem. Soc.*, 1947, 69, 1886.