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Synthesis and X-ray Structures of Cobalta-, Rhodia-, and Iridiacycloalkanes. Observation of Novel Structural Features in the Metallacyclopentane Rings

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The metallacycloalkanes (η^5-C$_5$Me$_5$M(CH$_2$)$_n$(PPh$_3$)) (M = Rh, n = 4–6; M = Ir, n = 4, 5) and (η^5-C$_5$H$_5$)Co(CH$_2$)$_4$(PPh$_3$) were prepared by the reaction of the alkylating reagents M'(CH$_2$)$_n$M' (M' = MgBr, Li) with the appropriate dihalogeno complexes and were characterized by elemental analysis, ^{1}H NMR and mass spectroscopy, and protolytic and bromolytic decomposition studies. The crystal structures of the rhodium (**1**), iridium (**4**), and cobalt (**6**) metallacyclopentanes were determined from X-ray diffractometer data and refined by least squares. The crystal data and the final R values are as follows: **1**, space group $P2_1/n$ (Z = 4), with cell parameters a = 12.422 (1) Å, b = 23.911 (2) Å, c = 9.308 (1) Å, β = 97.75 (2)°, R = 0.047; **4**, space group $P2_1/n$ (Z = 4), with cell parameters a = 12.423 (1) Å, b = 23.949 (2) Å, c = 9.344 (1) Å, β = 98.25 (2)°, R = 0.055; **6**, space group $P2_1/n$ (Z = 4), with cell parameters a = 16.018 (2) Å, b = 15.673 (2) Å, c = 8.977 (1) Å, β = 103.33 (2)°, R = 0.039. All the structural details are discussed with the special reference to the puckering of the metallacyclic rings and to the different locations of shorter than "normal" C–C bond distances in the metallacyclopentane moieties.

Introduction

The chemistry of the metallacycloalkane derivatives of the transition metals is an area of growing interest since it was recognized that these compounds could play an important role in a number of catalytic reactions such as olefin metathesis,[2] isomerization of strained carbocyclic rings,[3] [2 + 2] cycloaddition of olefins,[4–6] and oligomeriztion of 1,3-[7,8] and 1,2-dienes.[9–14]

Several metallacycles have already been isolated and a survey of their reactivity shows that this class of organometallic compounds exhibits unusual properties and undergoes unusual chemical transformations in comparison with acyclic dialkyl derivatives. These peculiarities allow a look toward interesting applications of metallacycles in organic and organometallic synthesis.

In this connection we have studied the synthesis of some group 8 metal metallacycles, and preliminary accounts on cobalt, rhodium, and iridium derivatives have been published.[15,16] We report now details of the preparation and characterization of these compounds together with the single-crystal X-ray diffraction analyses of the cobalt, rhodium,

and iridium metallacyclopentane derivatives. Unusual structural features—short carbon–carbon distances differently located in the metallacyclic moieties—have been observed which have no parallel in the previously reported structures of complexes of this type.

Experimental Section

All operations were done under N$_2$ or Ar by Schlenk techniques. Diethyl ether and tetrahydrofuran first were refluxed and distilled from sodium and then from lithium aluminum hydride. Pentane and benzene were washed free of olefins or thiophene with concentrated sulfuric acid, dried on calcium chloride, and then distilled from lithium aluminum hydride. Unless otherwise noted other solvents were reagent grade, and they were degassed under vacuum and dried on molecular sieves before use. CoI$_2$(PPh$_3$)(C$_5$H$_5$),[17] RhCl$_2$(PPh$_3$)(C$_5$Me$_5$),[18] IrCl$_2$(PPh$_3$)(C$_5$Me$_5$),[18] RhI$_2$(PPh$_3$)(C$_5$Me$_5$),[18] BrMg(CH$_2$)$_n$MgBr (n = 4–6),[19] Li(CH$_2$)$_4$Li,[20] and Mg(CH$_2$)$_4$[21] were prepared as described.

^{1}H NMR spectra were run at 100 MHz (JEOL) and at 60 MHz (Varian) by using Me$_4$Si as internal standard. Melting or decomposition points were determined with a Kofler hot-stage apparatus and are uncorrected. Molecular weights were determined at 37 °C by a Mechrolab vapor pressure osmometer (Model 3019). Mass spectra were obtained with a Varian MAT Model CH7 spectrometer. Microanalyses were performed by the Laboratorio di Microanalisi of the Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa. GLC analyses were performed on a Carlo Erba Fractovap Model GT or a Perkin-Elmer F 30 instrument equipped with flame ionization detectors.

(η^5-C$_5$Me$_5$)Rh(CH$_2$(CH$_2$)$_2$CH$_2$)(PPh$_3$) (**1**). **1** was prepared by reaction of **8** in tetrahydrofuran with **11** or alternatively by reaction of **7** with **14** in diethyl ether, according to previously reported procedures.[22] ^{1}H NMR (C$_6$D$_6$) δ 7.52–7.18 (m, 15, phenyl), 1.48 (d, J_{HP} = 2 Hz, 15, methyl), 1.40–0.70 (br m, 8, methylenes).

As previously described[22] **1** reacts with HCl(g) to give **7** and a mixture of n-butane (60%) and n-butenes (40%). Bromolysis of **1** in CCl$_4$ affords (η^5-C$_5$Me$_5$)RhBr$_2$(PPh$_3$) and 1,4-dibromobutane.

(η^5-C$_5$Me$_5$)Rh(CH$_2$(CH$_2$)$_3$CH$_2$)(PPh$_3$) (**2**). To a stirred suspension of **8** (0.4 g, 0.536 mmol) in Et$_2$O (80 mL) was added 7.5 mL (1.57 mmol) of a 0.21 M THF solution of **12** at room temperature.

(1) (a) Università di Pisa. (b) Istituto di Chimica delle Macromolecole del CNR. (c) Politecnico di Milano.
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The reaction mixture was stirred for a further 1.5 h and then filtered. An orange solution was obtained which, after removal of solvent under reduced pressure, gave a residue that was extracted with pentane (60 mL). The pentane extract was concentrated to 5 mL and chromatographed on a dry 15-cm column of alumina with use of pentane as the eluant. A yellow-orange band was collected that furnished orange crystals of **2** (0.1 g, yield 30%), which was crystallized from acetone at -30 °C (mp 109 °C dec). Anal. Calcd for $C_{33}H_{40}PRh$: C, 69.47; H, 7.07; M_r = 570.5. Found: C, 69.56; H, 7.29; M_r = 395 (osmometry in benzene). Mass spectral analysis gave a parent ion at m/e 570. ^1H NMR (acetone-d_6) δ 7.58–7.38 (m, 15, phenyl), 1.57 (dd, J_{HP} = 2.2 Hz, J_{HRh} = 0.45 Hz, 15, methyl), 1.40–0.57 (br m, 10, methylenes).

An ethereal solution of **2** (0.15 mmol in 20 mL of Et_2O) was treated at -70 °C with 2 mL of bromine (0.3 mmol). The temperature was raised to 20 °C, and, after the solution was stirred for 1.5 h, a microcrystalline solid was formed which was separated by filtration, washed with diethyl ether, and dried under vacuum. This compound was characterized as $(\eta^5\text{-}C_5Me_5)RhBr_2(PPh_3)$ (yield ca. 95%). The solution was washed with water, then with aqueous $Na_2S_2O_3$, and finally with water. GLC analysis revealed the presence of 1,5-dibromopentane along with unidentified products arising from side reactions of bromine with diethyl ether as it was proved by blank proofs.

Dry HCl was bubbled through a solution of **2** (0.15 mmol) in 1,3-dioxane (5 mL), at room temperature for 10 min. A rapid reaction took place with the formation of a red microcrystalline product which was identified as **7**. The solution was flash distilled under vacuum, and the volatile products were trapped at -190 °C. GLC analysis revealed the presence of *n*-pentane (30%), 1-pentene (45%), *cis*-2-pentene (16%), and *trans*-2-pentene (9%).

$(\eta^5\text{-}C_5Me_5)Rh(CH_2(CH_2)_4CH_2)(PPh_3)$ (3). This preparation was carried out as reported for **2**. From 0.408 g (0.54 mmol) of **8** and 7.2 mL (1.62 mmol) of a 0.22 M THF solution of **13** was obtained 0.16 g of **3** (yield 50%) as orange crystals, mp 107 °C dec. Anal. Calcd for $C_{34}H_{42}PRh$: C, 69.85; H, 7.24; M_r = 584.6. Found: C, 69.60; H, 7.50; M_r = 360 (osmometry in benzene). Mass spectral analysis gave a parent peak at m/e 584. ^1H NMR (acetone-d_6) δ 7.58–7.38 (m, 15, phenyl), 1.55 (dd, J_{HP} = 2.2 Hz, J_{HRh} = 0.45 Hz, 15, methyl), 1.40–0.50 (br m, 12, methylenes).

Treatment of an ethereal suspension of **3** with bromine followed by GLC analysis permitted the identification of 1,6-dibromohexane; the microcrystalline precipitate was identified as $(\eta^5\text{-}C_5Me_5)\text{-}RhBr_2(PPh_3)$.

Similarly, following treatment with anhydrous HCl, *n*-hexane (25%), 1-hexene (3%), *cis*-2-hexene (31%), *trans*-2-hexene (19%), *cis*-3-hexene (15%), and *trans*-3-hexene (7%) were detected. **7** was also isolated.

$(\eta^5\text{-}C_5Me_5)Ir(CH_2(CH_2)_2CH_2)(PPh_3)$ (4). To a stirred suspension of **9** (0.2 g, 0.3 mmol) in 60 mL of THF at room temperature was added over a period of 15 min 10 mL (0.95 mmol) of a 0.095 M solution of **11** in THF (or **15** in THF/dioxane). The reaction mixture was stirred for 3 h. The resulting yellow-orange solution was evaporated to an oil. The oily product was stirred with 35 mL of a pentane/benzene (2.5:1) mixture for 3 h at room temperature to give a yellow-green solution. After concentration at reduced pressure to 5 mL, the product was chromatographated under N_2 on a 10-cm column of alumina. The column was eluted with pentane, and a yellow-green band was collected as it eluted. The solution was evaporated to 10 mL, and then with cooling at -30 °C, 0.048 g (yield 25%) of yellow-green crystals of **4** was obtained; mp 209 °C dec. Anal. Calcd for $C_{32}H_{38}IrP$: C, 59.51; H, 5.93; M_r = 646.7. Found: C, 60.20; H, 6.10. Mass spectral analysis gave a parent ion at m/e 646. ^1H NMR (C_6D_6) δ 7.54–7.06 (m, 15, phenyl), 1.42 (d, J_{HP} = 2.0 Hz, 15, methyl), 2.00–1.66 (br m, 4, methylene), 1.40–1.00 (br m, 4, methylene).

Treatment of **4** (0.05 g, 0.077 mmol) in 5 mL of CCl_4 with 0.2 mL (4 mmol) of Br_2 at -78 °C and then 2 h at room temperature, followed by the usual workup, gave 1,4-dibromobutane (identified by GLC analysis) and quantitative amounts of $(\eta^5\text{-}C_5Me_5)IrBr_2(PPh_3)$, mp 275–280 °C dec. ^1H NMR ($CDCl_3$) δ 7.33–7.01 (m, 15, phenyl), 1.35 (d, J_{HP} = 2.0 Hz, 15, methyl).

Treatment with anhydrous HCl gave **9** and a mixture (identified by GLC analysis) of *n*-butane (96%), 1-butene (1%), and an unidentified product (3%).

$(\eta^5\text{-}C_5Me_5)Ir(CH_2(CH_2)_3CH_2)(PPh_3)$ (5). Following the same procedure reported for **4**, 0.2 g (0.3 mmol) of **9** in 6 mL of THF was reacted with 6 mL (0.9 mmol) of **12** to give 0.016 g (yield 8%) of pale yellow crystals of **5**, mp 188 °C dec. Anal. Calcd for $C_{33}H_{40}IrP$: C, 60.06; H, 6.11; M_r = 660.73. Found: C, 60.19; H, 6.17. Mass spectral analysis gave a parent ion at m/e 660. ^1H NMR (C_6D_6) δ 7.11–6.73 (m, 15, phenyl), 2.33–1.50 (br m, 6, methylene), 1.35 (d, J_{HP} = 2.3 Hz, 15, methyl), 1.33–0.72 (br m, 4, methylene).

Treatment of a solution of **5** (0.05 g, 0.077 mmol) in 5 mL of CCl_4 with 0.2 mL (4 mmol) of Br_2 at -78 °C and then 2 h at room temperature, followed by the usual workup, gave 1,5-dibromopentane (identified by GLC analysis) and quantitative amounts of $(\eta^5\text{-}C_5Me_5)IrBr_2(PPh_3)$.

Treatment with anhydrous HCl gave **9** and a mixture (identified by GLC analysis) of *n*-pentane (14%), 1-pentene (13%), 2-pentenes (67%), and an unidentified product (6%).

$(\eta^5\text{-}C_5H_5)Co(CH_2(CH_2)_2CH_2)(PPh_3)$ (6). To a suspension of **10** (0.3 g, 0.468 mmol) in diethyl ether (70 mL) was added, at room temperature, 10 mL of a THF solution of **11** (1.4 mmol) over a period of 45 min. The reaction mixture was stirred for a further 6 h, then the solvent was evaporated under vacuum, and the solid residue was extracted with pentane (80 mL). Removal of the solvent under vacuum left a red oil which was dissolved in benzene (2 mL) and then transferred to a dry 15-cm column of alumina which had been thoroughly flushed with N_2. The column was eluted with pentane, and an orange-red band was collected as it eluted. After removal of the solvent the red oily residue was dissolved in 3 mL of pentane. Cooling the resulting red solution to -30 °C gave 0.027 g (yield 15%) of red needles. Anal. Calcd for $C_{27}H_{28}CoP$: C, 69.56; H, 7.27. Found: C, 69.70; H, 7.29. ^1H NMR (acetone-d_6) δ 7.38 (m, 15, phenyl), 4.41 (s, 5, cyclopentadienyl protons), 1.5–0.6 (br m, 8, methylene).

X-ray Study of 1, 4, and 6. In all cases crystals suitable for X-ray diffraction measurements were obtained by slow crystallization from pentane. They are very stable at room temperature under N_2 atmosphere and can be stored for months at -30 °C. Exposure to air did not cause appreciable chemical change at least over a short period. The diffracted intensities were measured by means of a Philips PW 1100 four-circle diffractometer, using graphite-monochromated Mo $K\alpha$ radiation for **1** and **6** and Cu $K\alpha$ radiation for **4**. In all cases the ω–2θ scan technique was used, averaging two background counts for each reflection, with a background time of 2 × 10 s for **1** and **6** and of 2 × 40 s for **4**. The scan speeds of 2.4, 2.0, and 0.66°/min and the scan widths of 1.4, 1.0, and 1.1° for **1**, **4**, and **6**, respectively, were used. Intensity data were considered observed when $I > 2.5\sigma$ (σ^2 = peak counts + total background counts) and were corrected for the Lorentz and polarization effect; an absorption correction was applied only in the case of **4**, in view of the small linear absorption coefficients in the other cases.

The cell parameters listed below were refined by least-squares procedures using the accurately measured 2θ values of several strong reflections. Crystal data are as follows for the three crystals which are monoclinic with space group $P2_1/n$. **1**: $C_{32}H_{38}PRh$, M_r = 556.5, a = 12.422 (1) Å, b = 23.911 (2) Å, c = 9.308 (1) Å, β = 97.75 (2)°, V = 2739.4 Å^3, Z = 4, $F(000)$ = 1160, D_c = 1.343 g/cm^3, μ(Mo $K\alpha$) = 6.84 cm^{-1}. **4**: $C_{32}H_{38}PIr$, M_r = 645.8, a = 12.423 (1) Å, b = 23.949 (2) Å, c = 9.344 (1) Å, β = 98.25 (2)°, V = 2751.3 Å^3, Z = 4, $F(000)$ = 1288, D_c = 1.559 g/cm^3, μ(Cu $K\alpha$) = 99.39 cm^{-1}. **6**: $C_{27}H_{28}PCo$, M_r = 442.4, a = 16.018 (2) Å, b = 15.673 (2) Å, c = 8.977 (1) Å, β = 103.33 (2)°, V = 2193.0 Å^3, Z = 4, $F(000)$ = 928, D_c = 1.340 g/cm^3, μ(Mo $K\alpha$) = 8.97 cm^{-1}.

The structures of **1** and **6** were solved by the heavy-atom method; **4** was found to be isostructural with **1** on the basis of a comparison of the crystal data and the intensity distribution. The atomic scattering factors given by Cromer and Mann[23] were used with constant corrections in order to account for the anomalous scattering. The atomic positions were refined by least squares in the block-diagonal approximation. The thermal vibration parameters of the nonhydrogen atoms were refined isotropically in a first stage and then anisotropically. In the case of **1** and **6** the hydrogen atoms were located by difference-Fourier techniques and then refined by least squares with fixed isotropic thermal parameters. The major details of the experimental conditions and least-squares refinement are given in Table I. A list

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Table I. Details of the Experimental Conditions and Least-Squares Refinements

	1	4	6
measd reflctns	4745	4108	3437
obsd reflctns	2926	1977	2181
θ range, deg (d(min), Å)	2–25 (0.84)	3–60 (0.89)	3–24 (0.87)
approx cryst size, mm³	0.17 × 0.20 × 0.3	0.02 × 0.02 × 0.15	0.16 × 0.20 × 0.22
no. of isotropic least-squares cycles	4	5	4
no. of least-squares cycles with anisotropic thermal parameters	3	6	3
final R value	0.047	0.055	0.039
largest final shifts for nonhydrogen atoms	0.10σ	0.33σ	0.25σ

Scheme I. Preparation of Metallacycloalkanes
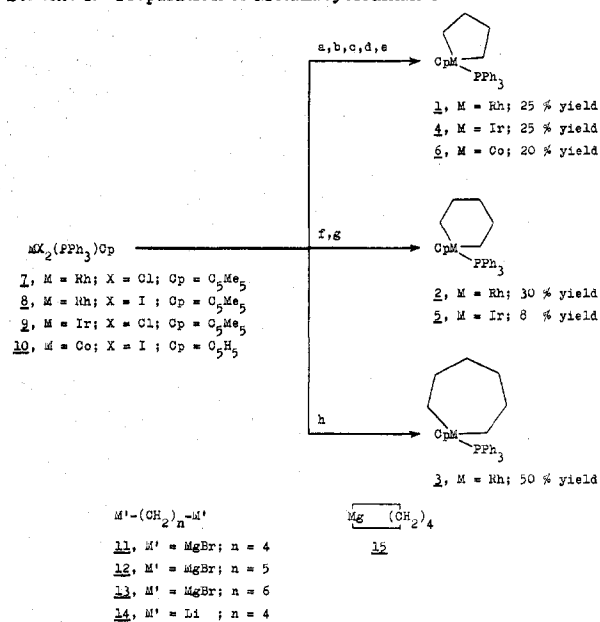
(a), 7 or 8 + 14, in Et₂O, at 0 °C; (b), 9 + 14, in Et₂O, at 0 °C; (c), 8 or 9 + 11, in THF, at room temp.; (d), 8 or 9 + 15, in THF, at room temp.; (e) 10 + 11, in Et₂O, at room temp.; (f), 8 + 12, in Et₂O, at room temp.; (g), 9 + 12, in THF, at room temp.; (h), 8 + 13, in Et₂O, at room temp.

of observed and calculated structure factors is available.[24]

Results and Discussion

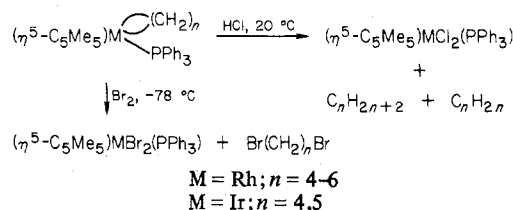**Preparation and Characterization of Cobalt, Rhodium, and Iridium Metallacycles.** Complexes 1–6 have been prepared by the reaction of the appropriate dihalogeno compounds with the alkylating reagents 11–15 (Scheme I).

This method has been successfully adopted for the synthesis of a number of metallacycloalkane derivatives of platinum-(II),[20] titanium(IV),[25] zirconium(IV),[25] nickel(II),[26] and palladium(II).[27]

(24) See paragraph at end of the paper regarding supplementary material.
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Scheme II. Reactions of Rhodium and Iridium Metallacycles with HCl and Br₂

The molar ratio alkylating reagent/transition metal was found to be critical: at values lower than 3, traces of metallacycles were obtained along with large amounts of unidentified halogenated metal compounds. The latter compounds were predominant when the reaction was carried out at temperatures lower than –20 °C. The effect of the reaction medium was also dramatic. Indeed, on reaction of a suspension of **8** in diethyl ether with **11** or **15**, a mixture of the rhodiacyclopentane derivative (**1**) and the ethylene complex, (η^5-C_5Me_5)Rh(C_2H_4)(PPh₃), was eventually obtained. A study on the formation of the latter compound as well as the details of the synthesis of pure **1** are reported elsewhere.[22] When the same reaction was carried out in tetrahydrofuran, pure **1** was obtained.

The reactions of the iridium dichloride (**9**) with the Grignard reagents **11**, **12**, or **15** proceeded easily at room temperature in tetrahydrofuran and gave the desired products **4** and **5**, while no reaction took place in diethyl ether. Many attempts to prepare the iridiacycloheptane derivative on reaction of **9** with **13** failed, leading to insoluble partially alkylated products.

At 37 °C, the molecular weights are those expected, with the exception of the ones found for the rhodiacyclohexane and rhodiacycloheptane derivatives that are about 30% lower, probably owing to the equilibrium

$$n = 5, 6$$
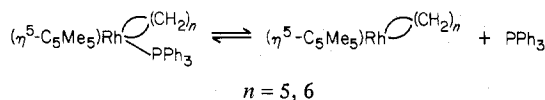
The mass spectra of **1–5** show parent peaks consistent with the appropriate molecular weights. The main fragmentation process is the one-step loss of the polymethylene moiety to give the base peak corresponding to $[C_5Me_5M(PPh_3)^+]$. In the mass spectrum of the cobalt metallacycle (**6**) the molecular ion is absent, the highest mass peak being the $[C_5H_5Co(PPh_3)^+]$ ion.

The ¹H NMR spectra of the metallacyclic compounds were dominated by the resonances of the ligands. Triphenylphosphine gives characteristic resonances, the C_5Me_5 ligand gives a double doublet in the case of compounds **1–5**, and the C_5H_5 ligand gives a singlet in the case of **6**. The coupling patterns are those expected for similar compounds.[18] As far as the polymethylene moiety is concerned, broad multiplets are present in the region of aliphatic protons whose integrated areas are consistent with the proposed formulations.

Since the complexity of the ¹H NMR spectra did not allow a conclusive confirmation of the structure, metallacycloalkanes **1–5** were also characterized by their reactions with HCl and bromine. Treatment of **1–5** with dry HCl yielded the corresponding complexes (η^5-C_5Me_5)MCl₂(PPh₃) and mixtures of *n*-alkanes and *n*-alkenes (Scheme II).

Treatment with bromine yielded 1,*n*-dibromoalkane in addition to (η^5-C_5Me)MBr₂(PPh₃); in the case of the complexes **1–3** [(η^5-C_5Me_5)RhBr₂]₂ was also found.

Crystal and Molecular Structures of 1, 4, and 6. The crystal structures of **1**, **4**, and **6** consist of the packing of discrete molecules with no intermolecular distance smaller than the sum of the commonly accepted van der Waals radii.

Table II. Fractional Atomic Coordinates of 1, 4, and 6[a]

	x/a	y/b	z/c		x/a	y/b	z/c
				1			
Rh	35421 (5)	15745 (2)	9008 (6)	C(11)	268 (7)	958 (4)	1719 (9)
P	22301 (15)	9408 (8)	4200 (20)	C(12)	701 (7)	1209 (4)	1967 (10)
C(1)	3392 (8)	1825 (4)	−1277 (9)	C(13)	−1043 (7)	1697 (4)	1287 (11)
C(2)	4388 (12)	1737 (7)	−1833 (14)	C(14)	−427 (7)	1949 (4)	348 (10)
C(3)	4808 (12)	1187 (5)	−1432 (16)	C(15)	554 (6)	1712 (3)	125 (9)
C(4)	4672 (7)	1029 (4)	142 (12)	C(20)	2400 (6)	292 (3)	1471 (7)
C(5)	3344 (6)	1837 (3)	3235 (8)	C(21)	3272 (6)	244 (3)	2564 (8)
C(5.1)	2643 (9)	1581 (5)	4247 (10)	C(22)	3439 (7)	−242 (4)	3359 (9)
C(6)	3032 (6)	2292 (3)	2316 (8)	C(23)	2745 (7)	−687 (4)	3070 (11)
C(6.1)	1982 (8)	2622 (4)	2268 (12)	C(24)	1880 (7)	−650 (3)	2011 (10)
C(7)	3951 (7)	2469 (4)	1666 (10)	C(25)	1708 (7)	−162 (3)	1200 (9)
C(7.1)	3990 (11)	2977 (4)	742 (13)	C(30)	1917 (6)	642 (3)	−1426 (8)
C(8)	4834 (6)	2102 (4)	2169 (10)	C(31)	2564 (7)	207 (4)	−1822 (9)
C(8.1)	5976 (8)	2186 (6)	1924 (15)	C(32)	2380 (7)	3 (4)	−3224 (10)
C(9)	4446 (6)	1719 (3)	3175 (9)	C(33)	1576 (8)	192 (4)	−4213 (10)
C(9.1)	5164 (10)	1313 (5)	4118 (12)	C(34)	929 (8)	618 (5)	−3838 (9)
C(10)	911 (6)	1212 (3)	774 (7)	C(35)	1109 (6)	845 (4)	−2451 (8)
				4			
Ir	35616 (7)	15771 (4)	9494 (11)	C(11)	307 (16)	953 (10)	1753 (23)
P	22499 (40)	9454 (22)	4559 (60)	C(12)	−696 (17)	1189 (11)	1968 (28)
C(1)	3444 (23)	1817 (10)	−1248 (25)	C(13)	−1036 (17)	1689 (11)	1298 (29)
C(2)	4500 (26)	1661 (22)	−1778 (30)	C(14)	−397 (20)	1939 (10)	379 (25)
C(3)	4904 (36)	1177 (15)	−1292 (54)	C(15)	612 (18)	1706 (9)	142 (26)
C(4)	4683 (18)	1010 (10)	241 (29)	C(20)	2417 (16)	310 (9)	1501 (21)
C(5)	3357 (20)	1844 (10)	3276 (24)	C(21)	3297 (18)	240 (9)	2611 (24)
C(5.1)	2621 (21)	1584 (12)	4261 (26)	C(22)	3437 (18)	−263 (9)	3386 (24)
C(6)	3043 (15)	2305 (9)	2343 (23)	C(23)	2746 (19)	−685 (9)	3040 (24)
C(6.1)	2005 (18)	2609 (12)	2262 (34)	C(24)	1845 (19)	−641 (8)	1984 (29)
C(7)	3954 (19)	2453 (9)	1720 (23)	C(25)	1695 (15)	−155 (9)	1212 (26)
C(7.1)	4009 (29)	2968 (10)	711 (28)	C(30)	1940 (15)	660 (8)	−1388 (22)
C(8)	4829 (19)	2106 (12)	2170 (25)	C(31)	2612 (18)	201 (10)	−1773 (26)
C(8.1)	5984 (22)	2177 (17)	1922 (37)	C(32)	2415 (22)	12 (11)	−3150 (23)
C(9)	4463 (17)	1705 (8)	3214 (24)	C(33)	1601 (19)	212 (12)	−4154 (24)
C(9.1)	5224 (25)	1326 (12)	4151 (35)	C(34)	925 (19)	639 (11)	−3806 (28)
C(10)	906 (15)	1209 (8)	766 (20)	C(35)	1108 (16)	860 (11)	−2413 (30)
				6			
Co	31355 (4)	21823 (4)	17113 (7)	C(14)	3120 (4)	192 (3)	5884 (7)
P	28255 (7)	25286 (7)	38328 (13)	C(15)	3233 (3)	930 (3)	5115 (6)
C(1)	4407 (3)	2048 (4)	2647 (6)	C(20)	1872 (3)	3206 (3)	3718 (5)
C(2)	4862 (4)	2666 (4)	1816 (7)	C(21)	1401 (3)	3483 (3)	2309 (6)
C(3)	4444 (4)	3490 (4)	1793 (8)	C(22)	677 (3)	3990 (3)	2192 (7)
C(4)	3465 (4)	3387 (3)	1281 (6)	C(23)	416 (3)	4201 (3)	3486 (7)
C(5)	1988 (4)	1522 (5)	858 (8)	C(24)	882 (3)	3956 (3)	4912 (7)
C(6)	2691 (5)	930 (4)	1209 (7)	C(25)	1618 (3)	3464 (3)	5029 (6)
C(7)	3215 (5)	1162 (5)	262 (8)	C(30)	3600 (3)	3144 (3)	5260 (5)
C(8)	2913 (5)	1832 (5)	−584 (7)	C(31)	3635 (3)	4023 (3)	5100 (5)
C(9)	2152 (4)	2053 (5)	−260 (7)	C(32)	4251 (3)	4507 (3)	6091 (6)
C(10)	2620 (3)	1581 (3)	4900 (5)	C(33)	4831 (3)	4117 (4)	7257 (6)
C(11)	1891 (3)	1450 (3)	5453 (5)	C(34)	4794 (3)	3255 (4)	7431 (6)
C(12)	1775 (3)	705 (4)	6201 (6)	C(35)	4182 (3)	2766 (3)	6445 (5)
C(13)	2396 (4)	82 (3)	6442 (6)				

[a] Esd's are in parentheses. The values are $\times 10^5$ for metal and phosphorus atoms and $\times 10^4$ for the other atoms.

While only the crystals of **1** and **4** are isomorphous to each other (see the crystal data), the molecules of the three complexes are almost isostructural, and for this reason we only give a view of **1** in Figure 1.

For the three crystal structures the fractional coordinates of all the refined atoms and the anisotropic thermal parameters of the nonhydrogen atoms are given in Tables II and III, respectively; selected bond distances and angles are reported in Tables IV and V. In all these tables the standard deviations estimated by the least-squares program are given in parentheses after the corresponding entries. In the case of the C–C(phenyl) and C–H average distances, for which the given standard deviations have been calculated on the basis of the formula $\sigma = [\sum_{i=1}^{n}(x_i = \bar{x})^2/(n-1)]^{1/2}$ ($\bar{x}$ is the average of the nx_i values of the considered distance); the reported small σ values constitute a proper basis for assessing the reliability of these structures.

The arrangement of the ligands about the metal atom can be described, according to Chruchill and Ni,[28] as a "three-legged piano stool" structure, with the legs constituted by the three σ bonds M–P, M–C(1), and M–C(4).

As for the cyclopentadienyl ring a survey of Table VI affords three major conclusions: (1) The Rh–C(C$_5$Me$_5$) and Ir–C-(C$_5$Me$_5$) average distances in **1** and **4** are very significantly longer than the corresponding average M–C(C$_5$Me$_5$) distances found in analogous complexes. (2) In **1** and **4** no significant differences are found in the M–C(C$_5$Me$_5$) (average values: 2.286 (24) Å for **1**; 2.27 (5) Å for **4**). (3) In the case of **6** one can observe an average Co–C(C$_5$H$_5$) distance (2.091 (8) Å) longer than that observed in Co(C$_5$H$_5$)(Ph$_2$C$_4$(Me$_3$Si)$_2$) (2.049 (7) Å)[29] and shorter than that observed in the cobal-

(28) Churchill, M. R.; Ni, W.-Y. S. *J. Am. Chem. Soc.* **1973**, *95*, 2150–2155.

Table III. Anisotropic Thermal Vibration Parameters of 1, 4, and 6[a]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
			1			
Rh	236 (2)	282 (2)	293 (2)	−43 (5)	128 (3)	−86 (5)
P	253 (8)	264 (8)	276 (8)	−23 (13)	65 (12)	−18 (13)
C(1)	67 (5)	57 (5)	37 (4)	−52 (9)	36 (8)	−4 (7)
C(2)	103 (9)	161 (14)	61 (7)	−48 (18)	70 (13)	23 (16)
C(3)	147 (11)	73 (7)	137 (11)	−33 (15)	26 (20)	−56 (14)
C(4)	31 (4)	59 (5)	80 (6)	−4 (7)	42 (8)	−63 (9)
C(5)	35 (4)	40 (4)	35 (4)	−21 (6)	11 (6)	−32 (6)
C(5.1)	82 (6)	61 (5)	42 (4)	−42 (11)	48 (8)	−29 (9)
C(6)	35 (4)	28 (3)	40 (4)	6 (5)	3 (6)	−21 (6)
C(6.1)	55 (5)	59 (6)	80 (7)	42 (9)	−8 (9)	−56 (10)
C(7)	48 (4)	32 (3)	42 (4)	−18 (6)	17 (6)	−17 (6)
C(7.1)	116 (9)	35 (4)	69 (6)	−52 (10)	38 (12)	2 (9)
C(8)	24 (3)	58 (5)	51 (5)	−18 (6)	14 (6)	−42 (8)
C(8.1)	33 (5)	130 (10)	118 (9)	−67 (11)	44 (10)	−148 (17)
C(9)	38 (4)	43 (4)	39 (4)	12 (6)	−27 (6)	−30 (6)
C(9.1)	81 (7)	66 (6)	65 (6)	30 (11)	−69 (11)	−14 (10)
C(10)	30 (3)	33 (3)	23 (3)	−2 (5)	−4 (5)	−5 (5)
C(11)	42 (4)	38 (4)	42 (4)	1 (6)	29 (6)	1 (6)
C(12)	47 (4)	51 (5)	57 (5)	3 (7)	55 (8)	−5 (8)
C(13)	34 (4)	63 (6)	68 (6)	21 (7)	20 (7)	−13 (9)
C(14)	36 (4)	39 (4)	55 (5)	25 (6)	12 (7)	5 (7)
C(15)	33 (3)	33 (4)	41 (4)	7 (5)	0 (6)	13 (6)
C(20)	40 (4)	25 (3)	24 (3)	3 (5)	16 (5)	−18 (5)
C(21)	43 (4)	29 (3)	35 (4)	6 (6)	6 (6)	−3 (6)
C(22)	41 (4)	49 (4)	39 (4)	20 (7)	−13 (6)	8 (7)
C(23)	47 (4)	35 (4)	64 (5)	19 (7)	22 (8)	13 (7)
C(24)	44 (4)	31 (4)	55 (5)	−13 (6)	23 (7)	−4 (7)
C(25)	43 (4)	28 (4)	45 (4)	−7 (6)	4 (6)	1 (6)
C(30)	34 (3)	34 (3)	25 (3)	−12 (6)	18 (5)	−11 (5)
C(31)	47 (4)	42 (4)	38 (4)	1 (7)	16 (6)	−25 (7)
C(32)	56 (5)	41 (4)	54 (5)	13 (7)	20 (8)	−29 (8)
C(33)	58 (5)	53 (5)	45 (4)	−27 (8)	−25 (7)	−42 (8)
C(34)	54 (5)	74 (6)	31 (4)	−10 (9)	−7 (7)	−4 (8)
C(35)	35 (4)	49 (4)	30 (4)	17 (6)	−8 (6)	−17 (6)
			4			
Ir	325 (2)	397 (3)	471 (3)	−62 (8)	160 (4)	−114 (10)
P	353 (22)	353 (23)	443 (27)	14 (38)	134 (38)	−20 (42)
C(1)	101 (16)	59 (14)	38 (10)	16 (23)	13 (21)	11 (19)
C(2)	107 (20)	335 (44)	57 (16)	−139 (52)	138 (30)	−126 (48)
C(3)	191 (30)	76 (17)	273 (35)	−69 (37)	360 (58)	−47 (41)
C(4)	41 (10)	60 (13)	90 (16)	12 (19)	32 (21)	2 (23)
C(5)	83 (13)	51 (12)	43 (11)	−26 (20)	−8 (19)	−25 (19)
C(5.1)	97 (15)	69 (12)	67 (13)	−115 (27)	68 (23)	−60 (26)
C(6)	30 (9)	43 (10)	59 (12)	7 (15)	4 (16)	−14 (18)
C(6.1)	38 (10)	86 (18)	133 (21)	10 (22)	16 (24)	−91 (33)
C(7)	61 (10)	39 (12)	39 (11)	−11 (16)	−9 (17)	−19 (18)
C(7.1)	181 (30)	30 (10)	53 (15)	−21 (27)	33 (32)	−12 (20)
C(8)	53 (13)	100 (17)	47 (15)	3 (23)	12 (20)	−14 (24)
C(8.1)	48 (11)	180 (29)	114 (21)	−68 (30)	27 (25)	−106 (41)
C(9)	50 (10)	41 (12)	60 (12)	43 (17)	−33 (18)	−18 (18)
C(9.1)	92 (18)	77 (17)	109 (20)	48 (28)	80 (31)	28 (30)
C(10)	43 (9)	37 (10)	36 (10)	−14 (15)	3 (15)	32 (15)
C(11)	38 (9)	64 (12)	50 (11)	−9 (18)	13 (17)	1 (17)
C(12)	33 (10)	96 (15)	74 (14)	−18 (20)	34 (19)	21 (25)
C(13)	42 (10)	68 (15)	95 (16)	22 (19)	33 (20)	5 (24)
C(14)	70 (13)	56 (13)	52 (12)	18 (21)	15 (19)	35 (20)
C(15)	55 (10)	40 (11)	73 (13)	3 (17)	7 (19)	−20 (19)
C(20)	48 (10)	47 (11)	37 (10)	41 (17)	28 (16)	−5 (17)
C(21)	61 (12)	31 (9)	57 (11)	−7 (18)	4 (19)	−3 (18)
C(22)	59 (12)	41 (10)	59 (13)	28 (18)	5 (20)	9 (19)
C(23)	67 (11)	43 (11)	46 (12)	−19 (19)	12 (20)	11 (18)
C(24)	65 (12)	19 (10)	95 (15)	−21 (17)	3 (21)	−22 (19)
C(25)	32 (9)	41 (10)	85 (14)	−4 (16)	2 (19)	−21 (20)
C(30)	33 (8)	39 (9)	49 (11)	−7 (15)	6 (15)	3 (16)
C(31)	53 (12)	58 (13)	66 (14)	−2 (21)	16 (21)	−51 (22)
C(32)	91 (15)	74 (15)	31 (10)	42 (24)	24 (21)	−20 (21)
C(33)	56 (12)	92 (14)	43 (12)	−55 (21)	−16 (19)	26 (22)
C(34)	54 (12)	79 (15)	71 (14)	5 (22)	−33 (21)	4 (24)
C(35)	31 (9)	75 (14)	87 (15)	1 (19)	3 (19)	−30 (25)
			6			
Co	296 (2)	341 (2)	288 (2)	28 (4)	96 (2)	−115 (4)
P	237 (4)	254 (4)	301 (4)	16 (6)	74 (6)	−34 (6)
C(1)	35 (2)	54 (3)	41 (2)	16 (4)	17 (4)	−6 (4)
C(2)	39 (3)	78 (4)	75 (4)	−13 (5)	16 (5)	3 (6)

. Table III (*Continued*)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(3)	64 (3)	52 (3)	95 (5)	−37 (5)	84 (6)	−19 (6)
C(4)	58 (3)	42 (3)	38 (2)	5 (4)	28 (4)	16 (4)
C(5)	59 (3)	115 (5)	9 (4)	−109 (7)	68 (6)	−142 (8)
C(6)	137 (6)	42 (3)	54 (3)	−68 (7)	−3 (7)	−27 (5)
C(7)	76 (4)	73 (4)	75 (4)	24 (6)	4 (6)	−94 (6)
C(8)	86 (4)	98 (5)	40 (3)	−37 (7)	36 (5)	−52 (6)
C(9)	67 (4)	77 (4)	59 (3)	24 (6)	−58 (5)	−53 (6)
C(10)	29 (2)	28 (2)	34 (2)	−8 (3)	6 (3)	−11 (3)
C(11)	35 (2)	40 (3)	40 (2)	−8 (4)	10 (4)	4 (4)
C(12)	47 (3)	48 (3)	46 (3)	−25 (4)	19 (4)	9 (4)
C(13)	66 (3)	34 (2)	42 (3)	−29 (4)	19 (5)	10 (4)
C(14)	60 (3)	33 (3)	60 (3)	14 (4)	12 (5)	11 (5)
C(15)	39 (2)	31 (2)	55 (3)	1 (4)	26 (4)	1 (4)
C(20)	26 (2)	27 (2)	41 (2)	−6 (3)	10 (3)	−12 (3)
C(21)	31 (2)	34 (2)	46 (2)	2 (3)	5 (4)	1 (4)
C(22)	34 (2)	35 (2)	67 (3)	14 (4)	−2 (4)	3 (4)
C(23)	35 (2)	34 (2)	87 (4)	18 (4)	24 (5)	−16 (5)
C(24)	42 (3)	41 (3)	67 (3)	2 (4)	52 (5)	−22 (5)
C(25)	35 (2)	33 (2)	45 (2)	−2 (3)	24 (4)	−17 (4)
C(30)	25 (3)	31 (4)	24 (3)	4 (3)	10 (3)	−3 (3)
C(31)	38 (2)	30 (2)	35 (2)	10 (3)	8 (3)	3 (3)
C(32)	41 (2)	32 (2)	51 (3)	−17 (4)	20 (4)	−19 (4)
C(33)	40 (3)	53 (3)	46 (3)	−22 (4)	6 (4)	−32 (4)
C(34)	37 (2)	55 (3)	38 (2)	6 (4)	−21 (4)	−4 (4)
C(35)	34 (2)	38 (2)	36 (2)	−4 (4)	3 (3)	3 (4)

^{a} Esd's are in parentheses. The values (in Å^2) are $\times 10^2$ for metal and phosphorus atoms and $\times 10$ for all the carbon atoms. The thermal function is $T = \exp[-(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)/4]$.

Table IV. Selected Interatomic Distances of 1, 4, and 6^a

	1	4	6
M–C(1)	2.098 (9)	2.117 (23)	2.027 (5)
M–C(2)	2.907 (15)	2.957 (38)	2.848 (7)
M–C(3)	2.995 (15)	3.015 (44)	2.920 (7)
M–C(4)	2.107 (10)	2.119 (25)	2.021 (5)
M–P	2.226 (2)	2.223 (5)	2.146 (1)
M–C(5)	2.306 (8)	2.315 (23)	2.095 (7)
M–C(6)	2.304 (8)	2.321 (21)	2.102 (6)
M–C(7)	2.289 (9)	2.249 (22)	2.084 (7)
M–C(8)	2.247 (8)	2.206 (24)	2.082 (6)
M–C(9)	2.284 (8)	2.268 (21)	2.090 (6)
C(1)–C(2)	1.420 (18)	1.513 (45)	1.509 (9)
C(2)–C(3)	1.445 (21)	1.318 (61)	1.454 (9)
C(3)–C(4)	1.545 (19)	1.549 (58)	1.540 (8)
C(5)–C(6)	1.407 (11)	1.426 (30)	1.437 (10)
C(5)–C(9)	1.406 (11)	1.423 (33)	1.375 (11)
C(6)–C(7)	1.426 (12)	1.392 (32)	1.375 (12)
C(7)–C(8)	1.434 (12)	1.386 (33)	1.321 (10)
C(8)–C(9)	1.439 (12)	1.485 (34)	1.361 (10)
C(5)–C(5.1)	1.497 (13)	1.521 (37)	
C(6)–C(6.1)	1.520 (13)	1.474 (31)	
C(7)–C(7.1)	1.493 (14)	1.558 (34)	
C(8)–C(8.1)	1.480 (13)	1.496 (38)	
C(9)–C(9.1)	1.514 (13)	1.499 (35)	
P–C(10)	1.833 (7)	1.847 (20)	1.839 (4)
P–C(20)	1.830 (7)	1.804 (21)	1.842 (5)
P–C(30)	1.853 (7)	1.842 (21)	1.838 (5)
phenyl (C–C)$_{av}$	1.380 (12)	1.391 (32)	1.382 (7)
M(CH$_2$)$_4$ (C–H)$_{av}$	1.01 (10)		1.05 (5)
Cp (C–H)$_{av}$			0.99 (6)
methyl (C–H)$_{av}$	0.99 (10)		
phenyl (C–H)$_{av}$	0.94 (8)		0.98 (4)

^{a} Esd's are in parentheses.

tacyclopentene complex   Co(CR^1=CR^{2}CHR^{2}CHR^2)- (PPh$_3$)(C$_5$H$_5$) (2.127 (12) Å).[30]

(29) Rausch, M. D.; Bernal, I.; Davis, B. R.; Sieger, A.; Higbie, F. A.; Westover, F. *J. Coord. Chem.* **1973**, *3*, 149–159.

Table V. Selected Bond Angles (Deg) and Torsion Angles (Deg) of 1, 4, and 6^a

	1	4	6
M–C(1)–C(2)	110.0 (7)	107.9 (17)	106.4 (3)
M–C(4)–C(3)	109.2 (7)	109.5 (17)	109.4 (3)
M–P–C(10)	111.8 (2)	112.8 (6)	111.4 (1)
M–P–C(20)	116.1 (2)	116.0 (6)	117.0 (1)
M–P–C(30)	120.4 (2)	119.7 (5)	119.6 (1)
C(1)–M–C(4)	80.2 (4)	80.1 (10)	84.0 (2)
C(1)–C(2)–C(3)	110.1 (11)	114.2 (29)	107.7 (5)
C(2)–C(3)–C(4)	112.7 (10)	115.9 (28)	110.3 (5)
C(5)–C(6)–C(7)	108.5 (6)	106.6 (17)	104.6 (6)
C(5)–C(9)–C(8)	108.1 (6)	105.3 (17)	109.4 (6)
C(6)–C(5)–C(9)	108.8 (6)	109.8 (17)	106.2 (6)
C(6)–C(7)–C(8)	107.5 (7)	111.7 (17)	111.8 (6)
C(7)–C(8)–C(9)	107.1 (6)	106.7 (18)	107.9 (6)
phenyl (C–C–C)$_{av}$	120.0 (6)	120.0 (16)	120.0 (4)

	$\sigma_{av}{}^b$		
av	1	3	1
M–C(1)–C(2)–C(3)	−46	−40	−49
M–C(4)–C(3)–C(2)	−16	−9	−24
C(1)–M–C(4)–C(3)	−7	−10	−3
C(2)–C(1)–M–C(4)	29	25	28

	$\sigma_{av}{}^b$		
	2	6	1
C(1)–C(2)–C(3)–C(4)	41	32	48

^{a} Esd's are in parentheses. ^{b} In the case of torsion angles the given σ are average values.

In the case of **6** the electron density does not appear to be fully delocalized, the C–C bond length sequence resembling the one typical of the localized form[31-33]

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Table VI. Comparison of M–C(Cp) Distances (Å) for 1, 4, and 6 and for Some Cobalt and Rhodium Cyclopentadienyls
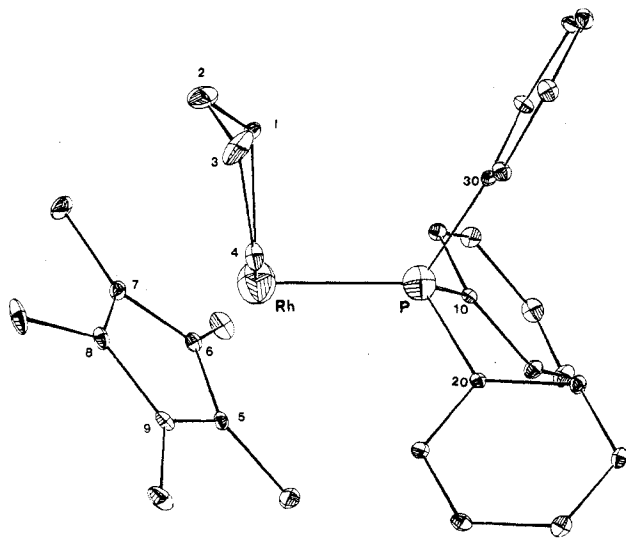
compd	M-C(Cp)					ref
	u	v	w	y	z	
$\overline{Rh(CH_2(CH_2)_2CH_2)}(PPh_3)(C_5Me_5)$ (1)	2.306 (8)	2.304 (8)	2.289 (9)	2.247 (8)	2.284 (8)	b
$\overline{Ir(CH_2(CH_2)_2CH_2)}(PPh_3)(C_5Me_5)$ (4)	2.315 (23)	2.321 (21)	2.249 (22)	2.206 (24)	2.268 (21)	b
$\overline{Co(CH_2(CH_2)_2CH_2)}(PPh_3)(C_5H_5)$ (6)	2.095 (7)	2.102 (6)	2.084 (7)	2.082 (6)	2.090 (6)	b
$Co(C_5H_5)(Ph_2C_4(Me_3Si)_2)$	2.053 (4)	2.057 (4)	2.049 (4)	2.042 (3)	2.042 (3)	29
$Rh(C_2H_4)(PPh_3)(C_5Me_5)$	2.266 (8)	2.230 (7)	2.288 (7)	2.266 (7)	2.230 (8)	32
$Rh(dba)(C_5Me_5)^a$	2.232 (6)	2.211 (6)	2.237 (6)	2.235 (6)	2.196 (6)	36
$Rh(C_2H_4)_2(C_5Ph_4Cl)$	2.183 (4)	2.299 (4)	2.305 (4)	2.271 (4)	2.254 (4)	31
$Rh(C_8H_{12})(C_5Cl_5)$	2.211 (6)	2.281 (4)	2.263 (4)	2.263 (4)	2.281 (4)	31
$Rh(C_2H_4)(C_2F_4)(C_5H_5)$	2.171 (6)	2.233 (6)	2.252 (6)	2.237 (7)	2.222 (6)	37
$\overline{Co(CR^1=CR^2CHR^2CHR^2)}(PPh_3)(C_5H_5)$	2.119 (14)	2.120 (11)	2.124 (11)	2.140 (14)	2.134 (15)	30

^{a} dba = PhCH=CHCOCH=CHPh. ^{b} This work.

Table VII. Comparison of C–C and M–C Distances (Å) of the Metallacyclic Ring for 1, 4, and 6 and for Analogous Rhodium and Iridium Complexes

compd	C-C			M-C		ref
	x	y	z	m	n	
$\overline{Rh(CH_2(CH_2)_2CH_2)}(PPh_3)(C_5Me_5)$ (1)	1.420 (18)	1.445 (21)	1.545 (19)	2.098 (9)	2.107 (10)	b
$\overline{Ir(CH_2(CH_2)_2CH_2)}(PPh_3)(C_5Me_5)$ (4)	1.51 (5)	1.32 (6)	1.55 (6)	2.117 (23)	2.119 (25)	b
$\overline{Co(CH_2(CH_2)_2CH_2)}(PPh_3)(C_5H_5)$ (6)	1.509 (9)	1.454 (9)	1.540 (8)	2.027 (5)	2.021 (5)	b
$\overline{Ir(CH_2C(=CH_2)C(=CH_2)CH_2)}(C_3H_4)(acac)py^a$	1.50 (4)	1.51 (4)	1.50 (4)	2.07 (3)	2.11 (2)	10
$Rh(CH_2C(=CH_2)C(=CH_2)CH_2)(acac)(py)_2,^a$	1.489 (20)	1.467 (20)	1.492 (20)	2.042 (10)	2.045 (10)	38
$Rh_2(C_6H_8)(acac)_2(PPh_3)_2^a$	1.510 (20)	1.435 (20)	1.503 (20)	2.078 (10)	2.085 (10)	38

^{a} acac = acetylacetonato and py = pyridine. ^{b} This work.

the shortening due to plausible rigid-body libration about the center of gravity of the cyclopentadienyl ring.[34]

The five-membered heterocyclic ring systems show two principal features, the puckering of the metallacyclic ring for which in all cases C(2) is closer to the metal than C(3) and the presence of some C–C bonds significantly shorter than the standard $C(sp^3)-C(sp^3)$ (Table VII). While a similar puckering was recently observed for two tetramethylene platinum complexes,[35] such short distances for the $C(sp^3)-C(sp^3)$ bonds of a metallacyclic ring have never been reported in the literature and constitute a common feature of the metallacycles **1**, **4**, and **6**, although the short C–C bonds are differently located in the three cases. Indeed the C–C bond length sequence in the metallacyclic moiety of **1** is asymmetric, the C(3)–C(4) distance being larger than the other two, while the sequence is different in **6** where the short C–C bond is symmetrically located between the longer C(1)–C(2) and C(3)–C(4) bonds. In **4** this sequence appears to be the same as in **6**, although the large standard deviations on the C–C

Figure 1. Computer drawing of **1** viewed along the normal to the plane formed by the Rh, P, and C(1) atoms. For the sake of clarity only the atoms relevant to the discussion (see text) are labeled.

A smaller degree of electron localization is also detectable in **1** and cannot be ruled out in **4**, even considering the large standard deviations. This evidence of electron localization becomes stronger after correcting the C–C bond lengths for

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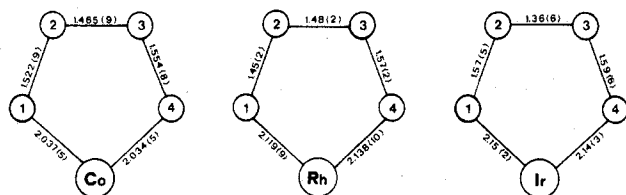
Figure 2. Bond lengths in the metallacyclopentane rings. The reported values are distances (Å) corrected for libration motion about the metal atom (see text).

distances in the iridiacycle do not allow one to be positive in this case. It may also be interesting to note that in **6** C-(1)–C(2) is probably shorter than C(3)–C(4), their difference being equal to 2.6σ. In principle, one cannot rule out the possibility that some of the observed shortening effect is an artifact created by the thermal motion of the carbon atoms in the rings. However, the results of a thermal motion analysis, performed by assuming a rigid-body libration about the metal atom,[34] left no doubts about the occurrence of the asymmetric C–C distance sequence in the rhodiacycle and about the reality of the other peculiar features of these cycles, at least in the case of **1** and **6** (Figure 2). In fact, in view of the possible torsional oscillations, suggested by the shape of the relevant thermal ellipsoids (Figure 1) and not taken into account by the assumed thermal motion model, the C(2)–C(3) bond lengths reported in Figure 2 should be considered as lower limits to the "true" values; nevertheless the fact that the relevant thermal parameters (Table III) are not unusually large and that, after the correction for rigid-body libration,

C(2)–C(3) is still significantly smaller than the adjacent C–C bonds indicates that these additional shortening effects cannot be large enough to justify the observed differences.

Even though the present evidence suggests, at least for the cobalt triad, a possible role of the metal in determining the C–C distance sequence in the metallacyclic rings (complexes **1** and **4** are isostructural, the only difference being the nature of the metal), the available data do not allow us to establish any clear correlation supporting this suggestion.

We would also like to point out the possible relevance of these findings to the carbon–carbon and carbon–hydrogen soft activation via transition-metal alkyls.

Registry No. 1, 63162-06-1; **2**, 63162-03-8; **3**, 63162-04-9; **4**, 66416-07-7; **5**, 74562-96-2; **6**, 74562-97-3; **7**, 63179-49-7; **8**, 32761-86-7; **9**, 66517-28-0; **10**, 42920-62-7; **11**, 23708-47-6; **12**, 23708-48-7; **13**, 17036-36-1; **14**, 2123-72-0; **15**, 26198-40-3; (η^5-C_5Me_5)RhBr$_2$(PPh$_3$), 63179-48-6; (η^5-C_5Me_5)IrBr$_2$(PPh$_3$), 74562-98-4; *n*-pentane, 109-66-0; 1-pentene, 109-67-1; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8; 1-hexene, 592-41-6; *cis*-2-hexene, 7688-21-3; *n*-hexane, 110-54-3; *cis*-3-hexene, 7642-09-3; *trans*-3-hexene, 13269-52-8; *trans*-2-hexene, 4050-45-7; *n*-butane, 106-97-8; 1-butene, 106-98-9; 1,5-dibromopentane, 111-24-0; 1,6-dibromohexane, 629-03-8; 1,4-dibromobutane, 110-52-1.

Supplementary Material Available: Listings of the observed and calculated structure factors and of the C–C(phenyl) distances for the three structures (85 pages). Ordering information is given on any current masthead page.

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Reactions of Aminophosphines with Carbon Dioxide, Carbonyl Sulfide, and Carbon Disulfide. Crystal and Molecular Structure of a Seven-Coordinate Tris(dithiocarbamato) Complex of Phosphorus(III)

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The room-temperature reactions of the aminophosphines [(CH$_3$)$_2$N]$_3$P, [(CH$_3$)$_2$N]$_2$PCl, [(CH$_3$)$_2$N]PF, (CH$_3$)$_2$NPCl$_2$, (CH$_3$)$_2$NPF$_2$, CH$_3$NCH$_2$CH$_2$N(CH$_3$)PCl, and CH$_3$NCH$_2$CH$_2$N(CH$_3$)PF with CO$_2$, COS, and CS$_2$ have been investigated. Several reactions proceed to products in which CO$_2$, COS, or CS$_2$ have undergone insertion in the P–N bonds. The products have been systematically characterized by mass, infrared, and multinuclear NMR spectrometries. The insertion product with the empirical molecular formula [(CH$_3$)$_2$N]$_3$P·3CS$_2$ has also been subjected to single-crystal X-ray structural analysis. The complex crystallizes in the monoclinic space group $P2_1/n$ with a = 7.180 (1) Å, b = 30.907 (6) Å, c = 16.300 (4) Å, β = 91.20 (2)°, Z = 8, V = 3616.4 (1) Å^3 and ρ = 1.44 g cm^{-3}. Diffraction data were collected with a Syntex P3/F automated diffractometer using Mo Kα radiation. The structure was solved by using MULTAN, and the full-matrix least-squares refinement converged with final discrepancy indices R_F = 0.066 and R_{wF} = 0.0101 on 4764 independent reflections. The crystals contain the discrete monomeric P–N bond insertion product tris(dithiocarbamato)phosphorus(III) (P[S$_2$CN(CH$_3$)$_2$]$_3$). The compound is formally seven-coordinate with the six sulfur atoms and the phosphorus atom lone pair forming a distorted capped trigonal antiprism. The PS$_6$ core has three short P–S bond lengths, 2.162 (3)–2.202 (3) Å, and three long P–S bond lengths, 2.873 (3)–3.016 (3) Å, with one short and one long P–S bond length associated with each planar dithiocarbamate ligand.

Introduction

The interactions of transition-metal complexes with small molecules such as N$_2$, O$_2$, NO, CO, CO$_2$, and SO$_2$ have recently attracted attention particularly within the context of catalytic conversion chemistry.[1] We have had an interest in

the interactions of several small molecules with coordinatively unsaturated metal complexes stabilized by multifunctional aminophosphines, and in the course of our work[2,3] we have found it necessary to obtain a better understanding of the

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(2) Light, R. W.; Paine, R. T. *Phosphorus Sulfur*, in press.
(3) A preliminary report on our results was presented earlier: Light, R. W.; Paine, R. T. "Abstracts of Papers", 34th Southwest Regional Meeting of the American Chemical Society, Corpus Christi, TX, 1978; American Chemical Society: Washington DC, 1978; INOR 7.