Synthesis of Cyclic Diamino-Substituted Metal Carbene Complexes

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A series of heterocyclic metal carbene complexes were prepared by the deoxygenation reaction of $M(CO)_6$ (M = Cr, Mo, W) with $RNH(CH_2)_nN=PPh_3$ (R = H, Et, Ph; n=2,3,4) to form the corresponding isocyanide complex, which subsequently underwent intramolecular cyclization to give (CO)₅M=CN(R)(CH₂)_nNH in good yields. None of the carbene complex reacted further with amine-phosphinimine RNH(CH₂)_nN=PPh₃ to give the bis(carbene) complex. Deprotonation of the N-H of the carbene complex followed by the reaction of alkyl iodides provided the N-alkylated product. In the case of N-allyl-substituted complexes $(CO)_5M=CNR(CH_2)_2N(CH_2CH=CH_2)$ (M = Cr, Mo, W), the carbon-carbon double bond underwent intramolecular ligand displacement of carbonyl ligand to yield the corresponding π -coordinated complex. Unlike the group VI metal carbonyl complexes, treatment of ReBr(CO)₅ with 2 molar equiv of Ph₃P=N(CH₂)₂NH₂ provided a bis(carbene) complex fac-(CO)₃BrRe(=CNHCH₂CH₂NH)₂. All complexes are characterized by both spectral and elemental analyses. Complexes (CO)₅Mo=CNHCH₂CH₂CH₂CH₂NH (**18**) and fac-(CO)₃BrRe-

 $(=\dot{C}NHCH_2CH_2\dot{N}H)_2$ (42) were further characterized by X-ray single-crystal analysis.

Introduction

One of the synthetic strategies for producing metal carbene complexes is nucleophilic addition to coordinated isocyanide ligands to form the corresponding carbene complex. While relevant examples applying this approach to prepare Pd(II), Pt(II), Zn(II), Au(I), Au(III), Co(III), and Rh(II) carbene complexes have been studied, 1-11 the reactivity of group VI metal carbonylisocyanide complexes toward nucleophiles has not been well explored. It was reported by Fehlhammer and coworkers that (CO)5CrCNCCl3 reacted with dithiols or diamines to yield the heterocyclic electron-rich carbene complex 1.6 It is also known that the stable aminosubstituted metal carbene species 1 (Z = NR) can be obtained by oxidative addition of tetraamino-substituted olefins or related species to metal carbonyl complexes.¹²

$$(CO)_5Cr-C\equiv N-CCl_3 \xrightarrow{HZ(CH_2)_2ZH} (CO)_5Cr = \stackrel{Z}{\swarrow} (1)$$

Recently, we reported that phosphinimine-phosphine Ph₃P=N(CH₂)₃PPh₂ (2) reacted with group VI metal carbonyls to yield two different type of products (Scheme 1) while the phosphine site of complex 3 remained uncoordinated.¹³ Here, we describe the replacement of the phosphine site of the phosphinimine 2 by a nitrogen donor and their activity in the formation of cyclic carbene complexes.

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Scheme 1

$$Et_4N^+[M(CO)_5Br] \\ PPh_2 \\ N \\ PPh_3 \\ PPh_3 \\ PPh_3 \\ M(CO)_6 \\ PPh_2 \\ M(CO)_4 \\ N \\ PPh_3 \\ PPh_2 \\ PPh_2 \\ N \equiv C-M(CO)_5 \\ 3$$

Scheme 2

Scheme 3

Results and Discussion

M = W.

M = Cr

M = Mo.

M = W.

M = W.

M = Cr

M = W

20 21

22

R = H.

R = H

R = H.

R = H

R = H

M = Mo, R = Et, n = 1

R = Et n = 1

R = Et. n = 1

R = Ph. n = 1

n = 1

n = 2

n = 3

Synthesis. A series of amino-phosphinimines (9– **13**) were prepared by the reaction of the corresponding azido compounds (4-8) with triphenylphosphine under extremely dry conditions which gave high yields (Scheme 2). All amino-phosphinimines were isolated as viscous liquids except 9, which was isolated as a white solid. Formulation of these phosphinimines was confirmed by spectral analysis. The ³¹P NMR shifts for phosphinimines were in the range of 10–15 ppm (relative to 85% H₃PO₄) typical for such functionality. Both infrared and ¹H NMR spectra show the NH moiety for the compounds.

Molar equivalents of $M(CO)_6$ (M = Cr, Mo, W) and phosphinimine 9 or 10 were reacted in dry tetrahydrofuran solvent with stirring at 25 °C (Scheme 3). Upon purification, all carbene complexes could be obtained as crystalline solids in good yields. Formation of the carbene complex had been expected via the deoxygenation of the carbonyl ligand by phosphinimine to form

Scheme 4

the isocyanide species, which is subsequently attacked by the amine moiety in an intramolecular fashion. 13,6 Both five- and six-membered rings of the carbene complexes can be obtained under mild conditions, but the reaction of **11** with W(CO)₆ under similar conditions only provided the isocyanide complex (CO)₅WCN(CH₂)₄-NH₂ (25) exclusively, which was isolated and characterized. This outcome is quite similar to the species (CO)₅CrCN(CH₂)₄NH₂ obtained from the reaction of (CO)₅CrCNCCl₃ with NH₂(CH₂)₄NH₂ by Fehlhammer and co-workers, 6a which did not undergo intramolecular cyclization to form the carbene species. However, complex 25 was slowly converted into the corresponding carbene complex 20 by addition of diethylamine in the reaction mixture.

When the nitrogen center became a secondary amine moiety, the nucleophilic attack at isocyanide to form carbene complexes still proceeded (Scheme 3). The present route to form diaminocarbene complexes is more versatile than the oxidative addition of amino-substituted olefins to metal centers. 12 In order to test the nucleophilicity of phosphinimine, a bis(phosphinimine) **26** was made to react with an equal molar amount of W(CO)₆. The reaction only provided a dinuclear isocyanide complex 27 (Scheme 4). It appears that the nitrogen center of phosphinimine did not undergo nucleophilic attack at isocyanide or carbonyl ligand intramolecularly, instead it reacted with another carbonyl ligand intermolecularly to form 27.

N-Alkylation and Ligand Substitution. The N-H moieties of carbene complexes are readily converted into the N-alkylated species by treatment of the complexes with excess of sodium hydride followed by alkylated agents. This procedure is quite similar to that reported by Angelici and co-worker.1c Thus a series of symmetrical and unsymmetrical diamino-substituted carbene complexes **28–35** were prepared by this method. In terms of alkylating reagents, it was found that the alkyl iodides were better than the corresponding bromides. The *N*-allyl-substituted metal carbene complexes readily underwent intramolecular ligand substitution to form π -bond coordinated species **36–39**. The

tungsten complex 32, as typical in refluxing THF solutions, provided the substituted product **39**. Due to geometrical constraints, the second allyl group of 35 does not coordinate to the metal center. Because of the same constraints on the proparagyl group, the π -bond coordinated species was not formed in **31**.

Bis(carbene) Complexes. Attempts to prepare the bis(carbene) species were unsuccessful. No reaction was observed when equal molar amounts of **18** and **9** were heated in refluxing THF; neither were the chromium and tungsten analogues formed. As discussed earlier, the formation of the carbene species requires the formation of isocyanide by the reaction of the phosphinimine with carbonyl ligand followed by the attack of an amine function. Apparently, the carbonyl ligands in **18** do not further react with phosphinimine to form isocyanide **40**.

This is consistent with our previous studies, which show that metal carbonlys $M(CO)_6$ (M=Cr,Mo,W) do not react with 2 molar equiv of phosphinimine 2 to yield bis(isocyanide) complexes. Analysis of the infrared absorptions of carbonyl ligands revealed that, upon carbene formation in metal complexes (carbene) $M(CO)_5$, the carbonyl stretching frequency shifted to smaller wavenumber. Such a shift is expected due to the weaker π -acceptor ability of carbene ligands, resulting in an increase in the strength of M-C back-bonding which reduces the electrophilic character of such carbon centers.

In our previous studies, the treatment of BrRe(CO)₅ with 2 equiv molar of phosphine—phosphinimine **2** yielded a bis(isocyanide) complex.¹³ Accordingly, the reaction of phosphinimine **9** with ReBr(CO)₅ provided the carbene complex **41**, which subsequently reacted

with another 1 equiv of **9** to give bis(carbene) complex **42**. This outcome confirms that the phosphinimine only reacts with highly electrophilic carbonyl ligands. Indeed, carbonyl stretching frequencies of **41** appeared at 2105, 2003, and 1916 cm⁻¹, which indicates a weak Re–C back-bonding interaction in **41** as compared to those in complexes of **14**–**24**. Thus the carbonyl ligand of **41** can be attacked by phosphinimine **9** to form a bis(carbene) complex.

Formulations of both rhenium complexes **41** and **42** were established by spectral and elemental analyses. Infrared and ¹³C NMR spectra clearly showed the metal carbonyl moieties and carbene carbon, respectively. The *facial* arrangement of **42** was proved by its carbonyl stretching pattern in the infrared spectrum and was further confirmed by an X-ray single-crystal structure.

Crystallography. Carbene complex **18** was obtained in a single-crystal form, and its structure was determined by the X-ray diffraction method. Figure 1 shows a perspective view of the complex whose selected bond

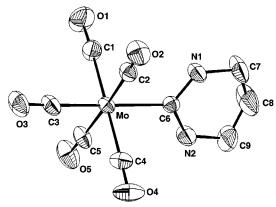


Figure 1. ORTEP plot of molybdenum carbene complex **18**.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for 18

Mo-C(1)	2.03(1)	C(1) - O(1)	1.14(1)
Mo-C(2)	2.03(1)	C(2) - O(2)	1.14(1)
Mo-C(3)	1.98(1)	C(3) - O(3)	1.15(1)
Mo-C(4)	2.02(1)	C(4) - O(4)	1.14(1)
Mo-C(5)	2.06(1)	C(5) - O(5)	1.13(1)
Mo-C(6)	2.26(1)	N(1)-C(7)	1.46(1)
C(6)-N(1)	1.31(1)	N(2)-C(9)	1.46(1)
C(6)-N(2)	1.31(1)		
Mo-C(6)-N(1)	123.2(4)	Mo-C(3)-O(3)	178.2(6)
Mo-C(6)-N(2)	122.8(4)	Mo-C(4)-O(4)	178.8(6)
Mo-C(1)-O(1)	175.8(6)	Mo-C(5)-O(5)	177.5(6)
Mo-C(2)-O(2)	176.6(6)		

distances and angles are reported in Table 1. As expected from the spectral analysis of 18, the metal is coordinated by the five carbonyl ligands and by the carbene ligand in an octahedral environment. All bond distances and bond angles lie within normal range. The shorter distance of Mo–C(3) [1.98(1) Å] is due to the *trans* influence of the carbene donor.

Examination of the dihedral angles along the chelate ring of **18** revealed two angles approaching 0° [C(7)– $N(1)-C(6)-N(2) 0.0^{\circ}$; $N(1)-C(6)-N(2)-C(9) 1.5^{\circ}$, typical of a half-chair-like six-member ring, indicating that the two nitrogen centers were in a planar geometry. This is consistent with the distances of carbon-nitrogen [1.31 (1) Å] being typical for C=N double bond. The distance of Mo-C(6) [2.262(6) Å] was significantly longer than that of the reported metal carbene species (CO)₅Mo= C(OR)SiPh₃ [2.15(2) Å]¹⁴ indicating that the metalcarbon bond had more single-bond characteristics. [The distance of Mo-C in Cp₂Mo(CO)CH₃ is 2.24 Å.] Dihedral angles N(2)-C(6)-Mo-C(4) and N(1)-C(6)-Mo-C(1) were 53.9(4) and 54.8(4)°, respectively. Thus the carbene moiety defined by plane of N(2)-C(6)-N(1) was staggered with the Mo(CO)₅ unit which is similar to that of the reported metal carbene species (CO)₅Mo= $C(OR)SiPh_3.^{14\bar{a},15}$

Slow evaporation of a dichloromethane/hexane solution of **42** yielded clear colorless crystals suitable for X-ray analysis. An ORTEP plot of **42** is illustrated in Figure 2, and selected bond distances and angles are listed in Table 2. The rhenium center displayed an octahedral geometry with one face occupied by the three carbonyl ligands. Bond lengths of $Re-C(4)[2.14(2)~\mbox{\normalfontA}]$

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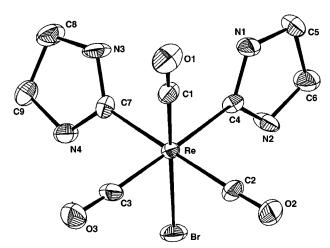


Figure 2. ORTEP plot of rhenium bis(carbene) complex **42**.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 42

Re-C(1) Re-C(2) Re-C(3) Re-C(4) Re-C(7) Re-Br C(1)-O(1)	1.88(2) 1.95(2) 1.91(2) 2.14(2) 2.17(2) 2.669(2) 1.14(2)	C(2)-O(2) C(3)-O(3) C(4)-N(1) C(5)-N(2) C(7)-N(3) C(7)-N(4)	1.13(2) 1.17(2) 1.36(2) 1.31(2) 1.32(2) 1.32(2)
Re-C(4)-N(1) Re-C(4)-N(2) Re-C(1)-O(1) Re-C(2)-O(2)	127(1) 129(1) 179(2) 178(2)	Re-C(3)-O(3) Re-C(7)-N(3) Re-C(7)-N(4)	177(2) 128(1) 125(1)

and Re-C(7) [2.17(2) Å] are typical for metal to carbene centers, and the small difference between them is believed to be due to the crystal packing since the spectral data for the two carbon centers are indistinguishable. The distance of Re-C(1) *trans* to bromide is slightly less than those *trans* to carbene ligands as expected, because of the *trans* influences.

Experimental Section

General Information. Nuclear magnetic resonance spectra were recorded in CDCl₃ on either a Bruker AC-E 200 or a AM-300 spectrometer. For ^{31}P NMR spectra, the chemical shifts are given in parts per million (δ) relative to 85% H_3PO_4 . Infrared spectra were measured on a Biorad FT-30 instrument. Infrared spectra were obtained on Biorad FT-IR instruments in CH_2Cl_2 solution, unless otherwise stated.

All of the reaction, manipulation, and purification steps involving phosphines were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. Benzene was distilled from sodium under nitrogen. Dichloromethane was dried by CaH₂ and then distilled under nitrogen. Other chemicals and solvents were used from commercial sources without further purification. Compounds $\bf 4-6$ were prepared by the method previously reported. 16a

N-(2-Azidoethyl)ethylamine (7). A solution of BrCH₂-CH₂NHEt·HBr^{16b} (3.0 g, 12.9 mmol) and sodium azide (2.5 g, 38.5 mmol) in water (50 mL) was heated to reflux for 12 h. The reaction mixture was neutralized with aqueous NaOH solution and extracted with ether (100 mL \times 2). After concentration of the organic extracts, the residue was distilled

under reduced pressure and trapped by liquid nitrogen to give the title compound as a colorless liquid (1.2 g, 82%): IR (neat) $\nu(N_3)$ 2101 cm⁻¹; 1H NMR δ 3.40 (t, J=5.8 Hz, 2 H), 2.76 (t, J=5.8 Hz, 2 H), 2.64 (q, J=7.1 Hz, 2 H), 1.46 (br, 1 H), 1.08 (t, J=7.1 Hz, 3 H); 13 C NMR δ 51.5, 48.2, 43.7, 15.2; HRMS calcd for C₄H₁₀N₄ $_m/e$ 114.0905, found $_m/e$ 114.0899.

N-(2-Azidoethyl)phenylamine (8). Preparation of this compound is similar to that of compound **6** except the starting material is Br(CH₂)₂NHPh·HBr.^{16c} A colorless liquid (82%) forms: IR (neat) ν (N₃) 2101 cm⁻¹; ¹H NMR δ 7.25–7.15 (m, 2 H), 6.82–6.63 (m, 3 H), 3.9 (br, 1 H), 3.52 (t, J = 5.5 Hz, 2 H), 3.38 (m, 2 H); ¹³C NMR δ 147.1, 129.3, 117.9, 112.9, 50.4, 42.9. HRMS calcd for C₈H₁₀N₄ m/e 162.0905, found m/e 162.0901.

General Procedure for Preparation of Amino-Phosphinimines. To a solution of azido-amine in benzene was added a solution of triphenylphosphine in benzene at 25 °C. The resulted mixture was stirred for 6 h. After removal of solvents, the desired product was obtained quantitatively (moisture sensitive). The preparation of 9 is described below as typical.

Ph₃P=N(CH₂)₂NH₂ (9). To a solution of azido compound **4** (2.0 g, 23.2 mmol) in dry benzene (50 mL) was added a solution of triphenylphosphine (6.1 g, 23.2 mmol) in benzene (50 mL). The resulting mixture was stirred at 25 °C for 6 h. After concentration of the reaction mixture, the residue was washed with hexane (2 mL \times 2). The desired product was obtained as a white solid (7.30 g, 98%): mp 103–104 °C; ¹H NMR δ 7.75–7.20 (m, 15 H), 3.13 (dt, ³ J_{P-H} = 16.5 Hz, J = 6.1 Hz, 2 H), 2.75 (dt, ³ J_{P-H} = 1.1 Hz, J = 6.1 Hz, 2 H), 1.85 (br, 2 H); ¹³C NMR δ (aliphatic) 48.5 (d, J_{P-C} = 5 Hz), 46.4 (d, J_{P-C} = 19 Hz); ³¹P NMR δ 13.4; HRMS calcd for m/e C₂₀H₂₁N₂P 320.1442, found m/e 320.1439.

Ph₃P=N(CH₂)₃NH₂ (10): Viscous liquid; ¹H NMR δ 7.65–7.24 (m, 15 H), 3.12 (dt, ³ $J_{\rm P-H}$ = 17.5 Hz, J = 6.7 Hz, 2 H), 2.71 (t, J = 6.4 H, 2 H), 1.65 (m, 2 H), 1.00 (br, 2 H); ¹³C NMR δ (aliphatic) 42.9(d, $J_{\rm P-C}$ = 6.5 Hz), 40.6, 39.0 (d, $J_{\rm P-C}$ = 17 Hz); ³¹P NMR δ 11.7; HRMS calcd for C₂₁H₂₃N₂P m/e 334.1599, found m/e 334.1578.

Ph₃P=N(CH₂)₄NH₂ (11): Viscous liquid; ¹H NMR δ 7.66–7.24 (m, 15 H), 3.06 (dt, ³ $J_{\rm P-H}$ = 18 Hz, J = 6.9 Hz, 2 H), 2.56 (t, J = 6.9 Hz, 2 H), 1.50 (m, 2 H), 1.40 (m, 2 H), 0.96 (br, 2 H, -NH); ¹³C NMR δ (aliphatic) 45.3 (d, $J_{\rm P-C}$ = 4.8 Hz), 42.2, 32.8 (d, $J_{\rm P-C}$ = 17.3 Hz), 31.7; ³¹P NMR δ 11.6; HRMS calcd for m/e C₂₂H₂₅N₂P 348.1755, found m/e 348.1749.

Ph₃P=N(CH₂)₂NH(CH₂CH₃) (12): Viscous liquid; ¹H NMR δ 7.70–7.25 (m, 15 H), 3.22 (dt, ³ J_{P-H} = 15.4, J = 6.0 Hz, 2 H), 2.75 (dt, ³ J_{P-H} = 1.1, J = 6.0 Hz, 2 H), 2.58 (q, J = 7.1 Hz, 2 H), 1.70 (br, 1 H), 1.04 (t, J = 7.1 Hz, 3 H); ¹³C NMR δ (aliphatic) 53.9 (d, J_{P-C} = 20 Hz), 44.7 (d, J_{P-C} = 5.1 Hz), 43.9, 15.4; ³¹P NMR δ 12.6; HRMS calcd for C₂₂H₂₅N₂P m/e 348.1755, found m/e 348.1749.

Ph₃P=N(CH₂)₂NHPh (13): Viscous liquid; ¹H NMR δ 7.70–7.32 (m, 15 H), 7.13 (m, 2 H), 6.61 (m, 3 H), 4.5 (br, 1 H), 3.38 (dt, ${}^3J_{P-H} = 16.7$, 5.8 Hz, 2 H), 3.23 (m, 2 H); ¹³C NMR δ (aliphatic) 47.5 (d, $J_{P-C} = 17.5$ Hz), 42.9 (d, $J_{P-C} = 4.7$ Hz); ³¹P NMR δ 14.4; HRMS calcd for C₂₆H₂₅N₂P m/e 396.1755, found m/e 396.1750.

General Procedure for Preparation of Carbene Complexes. A mixture of $M(CO)_6$ [M = Cr, Mo, W] and an equal molar amount of amino–phosphinimine in THF solution was stirred at 25 °C for 24 h. After concentration of the reaction mixture, the residue was chromatographed on silica gel with dichloromethane as the eluent. The eluate was concentrated, and the residue was recrystallized from a solution of chloroform and pentane to give the desired complex in crystalline solids. The preparation of 14 is described below as typical.

(CO)₅Cr=CNHCH₂CH₂NH (14). A mixture of Cr(CO)₆ (0.6 g, 2.73 mmol) and amine—phosphinimine **9** (0.88 g, 2.73 mmol) in dry tetrahydrofuran was stirred at 25 °C for 10 h. After removal of solvents, the residue was chromatographed on silica gel (10 g) with dichloromethane as the eluent. A light yellow band was collected and concentrated. The residue was re-

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crystallized from a solution of chloroform and pentane to give 14 as a light yellow crystalline solid (0.54 g, 76%): mp 106–107 °C [lit. 6a mp 105 °C]; IR (ν_{CO}) 2058, 1924 cm $^{-1}$; ^{1}H NMR δ 6.03 (br, 2 H), 3.62 (s, 4 H); ^{13}C NMR δ 221.8 (Cr=C), 221.2, 217.9, 44.9. Anal. Calcd for $C_8H_6N_2O_5Cr$: C, 36.66; H, 2.31; N, 10.69. Found: C, 36.54; H, 2.19; N, 10.53.

(CO)₅Mo=CNHCH₂CH₂NH (15). A light yellow solid formed (70%): mp 109–110 °C; IR (ν_{CO}) 2064, 1928 cm⁻¹; ¹H NMR δ 6.02 (br, 2 H), 3.59 (s, 4 H); ¹³C NMR δ 213.5 (Mo=C), 211.9, 206.6, 44.6. Anal. Calcd for C₈H₆N₂O₅CMo: C, 31.39; H, 1.98; N, 9.15. Found: C, 31.20; H, 2.01; N, 9.11.

(CO)₅**W=CNHCH**₂**CH**₂**NH (16).** A light yellow solid formed (87%): mp 129–130 °C; IR ($\nu_{\rm CO}$) 2064, 1921 cm⁻¹; ¹H NMR δ 5.97 (br, 2 H), 3.65 (s, 4 H); ¹³C NMR δ 204.0 (W=C), 201.8, 198.0, 45.1. Anal. Calcd for C₈H₆N₂O₅CW: C, 24.39; H, 1.53; N, 7.11. Found: C, 24.31; H, 1.42; N, 7.09.

(CO)₅Cr=CNH(CH₂)₃NH (17). A colorless solid formed (66%): mp 142–143 °C [lit.^{6a} mp 145 °C]; IR ($\nu_{\rm CO}$) 2055, 1921 cm⁻¹; ¹H NMR δ 6.03 (br, 2 H), 3.24 (dt, J = 2.4, 5.9 Hz, 4 H), 1.94 (quint, J = 5.9 Hz, 2 H); ¹³C NMR δ 221.7, 218.1, 214.8 (Cr=C), 40.7, 19.7. Anal. Calcd for C₉H₈N₂O₅Cr: C, 39.14; H, 2.92; N, 10.14. Found: C, 38.92; H, 2.82, N, 10.07.

(CO)₅**Mo=CNH(CH**₂**)**₃**NH (18).** A light yellow solid formed (64%): mp 139–141 °C; IR ($\nu_{\rm CO}$) 2063, 1924 cm⁻¹; ¹H NMR δ 5.96 (br, 2 H), 3.22 (dt, J = 2.5, 5.9 Hz, 4 H), 1.95 (quint, J = 5.9 Hz, 2 H); ¹³C NMR δ 212.1, 208.9 (Mo=C), 206.9, 40.2, 19.7. Anal. Calcd for C₉H₈N₂O₅Mo: C, 33.77; H, 2.52; N, 8.75. Found: C, 33.78; H, 2.49; N, 8.51.

(CO)₅W=CNH(CH₂)₃NH (19). A light yellow solid formed (84%): mp 164–165 °C; IR ($\nu_{\rm CO}$) 2062, 1917 cm⁻¹; ¹H NMR δ 5.98 (br, 2 H), 3.23 (dt, J = 2.4, 5.9 Hz, 4 H), 1.98 (quint, J = 5.9 Hz, 2 H); ¹³C NMR δ 202.0, 199.2 (W=C), 198.9, 40.5, 19.4. Anal. Calcd for C₉H₈N₂O₅W: C, 26.49; H, 1.98; N, 6.87. Found: C, 26.38; H, 1.92; N, 6.78.

(CO)₅W=CNH(CH₂)₄NH (20). Complex **25** (0.80 g, 1.90 mmol) in diethylamine (20 mL) was stirred for 48 h. After concentration of the reaction mixture, the residue was chromatographed on silica gel with dichloromethane as the eluent. A yellow band was collected and concentrated to give **20** as a yellow solid (51%): mp 117–118 °C; IR (ν_{CO}) 2064, 1918 cm⁻¹; ¹H NMR δ 6.07 (br, 2 H, N*H*), 3.42 (m, 4 H), 1.94 (m, 4 H); ¹³C NMR δ 202.0, 199.0, 194.2 (W=C), 46.4, 26.7. Anal. Calcd for C₁₀H₁₀N₂O₅W: C, 28.46; H, 2.39; N, 6.64. Found: C, 28.53; H, 2.27; N, 6.55.

(CO)₅Cr=CN(CH₂CH₃)CH₂CH₂NH (21). A yellow crystalline solid formed (55%): mp 75–76 °C; IR ($\nu_{\rm CO}$) 2056, 1923 cm⁻¹; ¹H NMR δ 5.68 (br, 1 H), 3.73 (q, J = 7.2 Hz, 2 H), 3.57 (m, 4 H), 1.26 (t, J = 7.2 Hz, 3 H); ¹³C NMR δ 221.8, 219.2 (Cr=C), 218.0, 47.8, 45.1, 44.5, 13.4. Anal. Calcd for C₁₀H₁₀N₂O₅Cr: C, 41.39; H, 3.47; N, 9.65. Found: C, 41.37; H, 3.51; N, 9.36.

(CO)₅Mo=CN(CH₂CH₃)CH₂CH₂NH (22). A yellow solid formed (64%): mp 80–81 °C; IR (ν_{CO}) 2064, 1927 cm⁻¹; ¹H NMR δ 5.62 (br, 1 H), 3.70 (q, J = 7.1 Hz, 2 H), 3.57 (m, 4 H), 1.24 (t, J = 7.1 Hz, 3 H); ¹³C NMR δ 213.7 (Mo=C), 212.0, 206.7, 47.1, 45.8, 44.9, 13.5. Anal. Calcd for C₁₀H₁₀N₂O₅Mo: C, 35.95; H, 3.02; N, 8.38. Found: C, 36.17; H, 2.90; N, 8.32.

(CO)₅**W=CN(CH**₂**CH**₃**)CH**₂**CH**₂**NH (23).** A yellow solid formed (96%): mp 96–97 °C; IR (ν_{CO}) 2063, 1930 cm⁻¹; ¹H NMR δ 5.65 (br, 1 H), 3.70 (q, J = 7.2 Hz, 2 H), 3.57 (m, 4 H), 1.25 (t, J = 7.2 Hz, 3 H); ¹³C NMR δ 204.7 ($J_{\text{P-W}}$ = 91.4 Hz) (W=C), 201.6 ($J_{\text{P-W}}$ = 131.4 Hz), 198.1 ($J_{\text{P-W}}$ = 125.5 Hz), 47.1, 46.6, 45.1, 13.5. Anal. Calcd for C₁₀H₁₀N₂O₅W: C, 28.46; H, 2.39; N, 6.64. Found: C, 27.95; H, 2.28; N, 6.50.

(CO)₅W=CN(Ph)CH₂CH₂NH (24). A light yellow solid formed (78%): mp 95–96 °C; IR (ν_{CO}) 2064, 1926 cm⁻¹; ¹H

NMR δ 7.48–7.29 (m, 5 H), 6.15 (br, 1 H), 3.94 (m, 2 H), 3.79 (m, 2 H); 13 C NMR δ 207.4 (W=C), 201.6, 197.9, 142.5, 129.6, 128.5, 128.1, 53.6, 45.7. Anal. Calcd for $C_{14}H_{10}N_2O_5W$: C, 35.77; H, 2.14; N, 5.96. Found: C, 34.11; H, 2.33; N, 6.25.

(CO)₅**WCN(CH**₂)₄**NH**₂ **(25).** A mixture of W(CO)₆ (1.28 g, 3.64 mmol) and **11** (1.27 g, 3.64 mmol) in THF (50 mL) was stirred at 25 °C for 48 h. The reaction mixture was concentrated, and the residue was chromatographed on silica gel with acetone as the eluent. A yellow band was collected and concentrated to give **25** as a yellow liquid (57%): IR (ν_{NC}) 2177 cm⁻¹, (ν_{CO}) 2068, 1945 cm⁻¹; ¹H NMR δ 3.67 (t, J = 6.5 Hz, 2 H), 2.77 (t, J = 6.8 Hz, 2 H), 1.82 (m, 2 H), 1.61 (m, 2 H), 1.50 (br, 2 H); ¹³C NMR δ 196.3, 194.3, 142.1 (CN-), 44.1, 41.0, 30.1, 26.6. Anal. Calcd for C₁₀H₁₀N₂O₅W: C, 28.46; H, 2.39; N, 6.64. Found: C, 28.30; H, 2.59; N, 6.47.

Ph₃P=N(CH₂)₄N=PPh₃ (26). The preparation of **26** is similar to the method described for **9** except N₃(CH₂)₄N₃¹⁸ was used. A white solid formed (99%): mp 112–113 °C (dec); ¹H NMR δ 7.64–7.26 (m, 30 H), 3.05 (m, 4 H), 1.58 (m, 4 H); ¹³C NMR δ (aliphatic) 45.70 (d, $J_{P-C} = 5.3$ Hz), 33.63 (d, $J_{P-C} = 16.7$ Hz); ³¹P NMR δ 10.64.

(CO)₅WCN(CH₂)₄NCW(CO)₅ (27). A mixture of **26** (4.1 g, 6.9 mmol) and W(CO)₆ (2.37 g, 6.7 mmol) in THF was stirred at 25 °C for 48 h. After the concentration of the reaction mixture, the residue was chromatographed on silica gel with dichloromethane as the eluent. A yellow band was collected and concentrated to give **27** as a yellow solid (43%): mp 112–113 °C (dec); IR ($\nu_{\rm CN}$) 2171 cm⁻¹, ($\nu_{\rm CO}$) 2066, 1948 cm⁻¹; ¹H NMR δ 3.78 (m, 4 H), 1.94 (m, 4 H); ¹³C NMR δ 195.9, 194.1, 144.6 (–N*C*), 43.4, 26.3. Anal. Calcd for C₁₆H₈N₂O₁₀W₂: C, 25.42; H, 1.07; N, 3.71. Found: C 25.34; H, 1.09; N, 3.57.

General procedures for N-Alkylation. To a solution of diamino-substituted carbene complex in THF was added an excess of sodium hydride with stirring overnight. The alkylating agent was then added to the reaction mixture and kept stirring for another 8 h. Water was added at ice-cooled temperature to quench the reaction. The organic layer was separated, dried, and concentrated. The residue was chromatographed on silica gel with dichloromethane as the eluent. A light yellow band was collected and concentrated to give the desired alkylated product. The preparation of 28 is described below as typical.

 $(CO)_5Cr=CN(CH_2CH_3)CH_2CH_2N(CH_2CH_3)$ (28). A mixture of 14 (700.0 mg, 2.67 mmol) and sodium hydride (0.3 g, 12.5 mmol) in THF was stirred for 24 h. Ethyl iodide (0.98 g, 6.3 mmol) was then added, and the reaction mixture was stirred for another 8 h. Water (5 mL) was added to quench the sodium hydride at ice-cooled temperature. The organic layer was separated, dried, and concentrated. The residue was chromatographed on silica gel with dichloromethane as the eluent. A light yellow band was collected and concentrated to give the desired alkylated product 28 as a light yellow solid (0.64 g, 75%): mp 99-100 °C [lit.12a mp 100-102 °C]; IR($\nu_{\rm CO}$) 2054, 1929 cm⁻¹; ¹H NMR δ 3.82 (q, J = 7.1 Hz, 4 H), 3.51 (s, 4 H), 1.24 (t, J = 7.1 Hz, 6 H); ¹³C NMR δ 222.1, 219.2 (Cr=C), 217.9, 47.7, 46.0, 13.6. Anal. Calcd for C₁₂H₁₄N₂O₅-Cr: C, 45.29; H, 4.43; N, 8.80. Found: C, 45.15; H, 4.32; N, 8.75.

(CO)₅Mo=CN(CH₂CH₃)CH₂CH₂N(CH₂CH₃) (29). A light yellow solid formed (73%): mp 92–93 °C [lit. 12b mp 93 °C]; IR ($\nu_{\rm CO}$) 2063, 1928 cm $^{-1}$; 1 H NMR δ 3.78 (q, J=7.2 Hz, 4 H), 3.53 (s, 4 H), 1.22 (t, J=7.2 Hz, 6 H); 13 C NMR δ 214.1 (Mo=C), 212.2, 206.5, 47.6, 46.4, 13.5. Anal. Calcd for C₁₂H₁₄N₂O₅Mo: C, 39.79; H, 3.90; N, 7.73. Found: C, 39.48; H, 3.94; N, 7.88.

(CO)₅W=CN(CH₂CH₃)CH₂CH₂N(CH₂CH₃) (30). A light yellow solid (87%): mp 99–100 °C [lit.^{12c} mp 102 °C]; IR (ν_{CO}) 2062, 1919 cm⁻¹; ¹H NMR δ 3.78 (q, J = 7.2 Hz, 4 H), 3.56 (s,

⁽¹⁸⁾ Svetlakov, N. V.; Mikheev, V. V.; Fedotov, Yu. A. Zh. Org. Khim. 1971, 7, 2220.

Table 3. Crystal Data for Complexes 18 and 42

	compd	
	18	42
formula	C ₉ H ₈ N ₂ O ₅ Mo	C ₉ H ₁₂ BrN ₄ O ₃ Re
fw	320.11	490.33
cryst syst	orthorhombic	triclinic
space group	$P2_12_12_1$	$P\bar{1}$
temp, K	298	298
a, Å	6.101(3)	7.355(2)
b, Å	13.339(5)	8.241(3)
c, Å	15.557(6)	13.492(3)
α, deg		73.32(2)
β , deg		74.18(3)
γ, deg		63.66(3)
V, Å ³	1266.1(9)	691.9(3)
2θ range, deg	22.60-31.72	15.72-37.00
F(000)	632	456
$\mathbf{Z}^{}$	4	2
$D_{ m calcd}$, g cm $^{-3}$	1.679	2.354
μ , cm ⁻¹	10.198	117.674
scan width	ω -2 θ	ω -2 θ
radiation	Μο Κα	Μο Κα
cryst dimens, mm	0.30 imes 0.35 imes 0.50	$0.20 \times 0.20 \times 0.50$
scan width	$2(1.00 + 0.35 \tan \theta)$	$2(0.70 + 0.35 \tan \theta)$
transm range	0.939; 1.00	0.787; 1.00
2θ max, deg	50.0	45.0
no. of unique reflns	1316	1804
no. of reflns obsda	1209	1664
computation	NRCSDP-VAX	NRCSDP-VAX
soln method	heavy atom	heavy atom
no. of params	155	164
R	0.025	0.035
$R_{\rm w}$	0.027	0.055
S	2.77	2.03
-	~	æ.00

 $^{a}I > 2\sigma(I)$. $^{b}R = \sum |F_{0} - F_{c}|/\sum(F_{0})$; $R_{w} = [\sum w(F_{0} - F_{c})^{2}/\sum(wF_{0})^{2}]^{1/2}$; $S = [\sum w(F_{0} - F_{c})^{2}/(\text{no. of reflns - no. of params})]$.

Table 4. Atomic Coordinates and Isothermal Parameters (Ų) for 18

	X	у	Z	$B_{ m eq}$
Mo	0.80545(8)	0.36484(4)	0.20423(3)	3.755(23)
C(1)	0.6198(11)	0.4147(5)	0.3037(5)	5.6(3)
C(2)	1.0234(12)	0.4766(5)	0.2269(4)	4.7(3)
C(3)	0.9774(14)	0.2809(5)	0.2844(5)	5.7(4)
C(4)	0.9822(12)	0.3137(5)	0.1035(5)	5.5(4)
C(5)	0.5832(12)	0.2510(5)	0.1860(5)	5.5(4)
C(6)	0.6224(10)	0.4660(4)	0.1123(4)	3.9(3)
C(7)	0.4877(15)	0.6337(5)	0.0683(6)	8.8(5)
C(8)	0.3532(24)	0.5867(6)	0.0085(7)	15.1(9)
C(9)	0.4057(19)	0.4915(6)	-0.0208(5)	9.4(6)
N(1)	0.6034(10)	0.5628(3)	0.1236(3)	5.7(3)
N(2)	0.5245(12)	0.4326(4)	0.0430(4)	7.0(4)
O(1)	0.5229(11)	0.4392(5)	0.3628(3)	9.5(4)
O(2)	1.1484(9)	0.5368(4)	0.2433(3)	7.5(3)
O(3)	1.0757(10)	0.2336(4)	0.3328(4)	8.1(3)
O(4)	1.0816(10)	0.2832(4)	0.0473(3)	8.7(3)
O(5)	0.4640(9)	0.1869(4)	0.1788(4)	8.2(3)

4 H), 1.23 (t, J = 7.2 Hz, 6 H); ¹³C NMR δ 205.6 (W=C), 201.6, 198.0, 47.4, 47.3, 13.4. Anal. Calcd for $C_{12}H_{14}N_2O_5W$: C, 32.02; H, 3.14; N, 6.22. Found: C, 31.84; H, 3.03; N, 6.18.

(CO)₅W=CN(CH₂CH₃)CH₂CH₂N(CH₂CCH) (31). A yellow solid formed (86%): mp 93–94 °C; IR (ν_{CO}) 2064, 1920 cm⁻¹; ¹H NMR δ 4.58 (d, J = 2.5 Hz, 2 H), 3.82 (q, J = 7.2 Hz, 2 H), 3.64 (m, 4 H), 2.35 (t, J = 2.5 Hz, 1 H), 1.25 (t, J = 7.2 Hz, 3 H); ¹³C NMR δ 207.4 (W=C), 201.1, 197.5, 77.6, 73.9, 47.8, 47.6, 42.8, 13.4. Anal. Calcd for C₁₃H₁₂N₂O₅W: C, 33.94; H, 2.63; N, 6.09. Found: C, 33.85; H, 2.46; N, 6.16.

(CO)₅W=CN(CH₂CH₃)CH₂CH₂N(CH₂C=CH₂) (32). A yellow solid formed (85%): IR ($\nu_{\rm CO}$) 2063, 1920 cm⁻¹; ¹H NMR δ 5.81 (m, 1 H), 5.26 (m, 2 H), 4.33 (d, J = 6.1 Hz, 2 H), 3.80 (q, J = 7.2 Hz, 2 H), 3.53 (m, 4 H), 1.25 (t, J = 7.2 Hz, 3 H); ¹³C NMR δ 206.7 ($J_{\rm C-W}$ = 95 Hz) (W=C), 201.4 ($J_{\rm C-W}$ = 129.8 Hz), 197.9 ($J_{\rm C-W}$ = 125.7 Hz), 133.1, 118.9, 55.6, 47.9, 47.5, 47.4,

Table 5. Atomic Coordinates and Isothermal Parameters (Ų) for 42

	X	y	Z	$B_{ m eq}$
Re	0.24517(10)	0.19503(9)	0.23993(5)	2.52(3)
\mathbf{Br}	0.1616(3)	0.3760(3)	0.28683(16)	4.35(11)
N(1)	0.4373(20)	0.4923(20)	0.1466(12)	3.8(8)
N(2)	0.1168(21)	0.6176(19)	0.1465(14)	4.6(8)
N(3)	0.4198(23)	0.254(3)	0.4091(12)	4.9(11)
N(4)	0.1303(23)	0.2354(24)	0.4743(11)	4.3(10)
C(1)	0.531(3)	0.0673(25)	0.2061(13)	3.5(9)
C(2)	0.208(3)	0.184(3)	0.1045(14)	4.3(11)
C(3)	0.221(3)	-0.034(3)	0.3070(14)	3.9(11)
C(4)	0.2642(23)	0.4568(20)	0.1734(12)	2.4(8)
C(5)	0.407(3)	0.6830(24)	0.1016(15)	3.9(10)
C(6)	0.176(3)	0.774(3)	0.1003(17)	5.0(12)
C(7)	0.2687(25)	0.2323(22)	0.3878(12)	3.1(8)
C(8)	0.385(3)	0.284(3)	0.5150(16)	5.2(13)
C(9)	0.187(3)	0.259(3)	0.5634(14)	4.5(11)
O(1)	0.7048(21)	-0.0121(21)	0.1853(11)	5.8(8)
O(2)	0.190(3)	0.1815(22)	0.0244(10)	6.0(10)
O(3)	0.2109(24)	-0.1747(20)	0.3509(11)	5.7(9)

13.5. Anal. Calcd for $C_{13}H_{14}N_2O_5W$: C, 33.79; H, 3.05; N, 6.06. Found: C, 33.92; H, 2.87; N, 6.02.

(CO)₅Cr=CN(CH₂CH=CH₂)CH₂CH₂N(CH₂CH=CH₂) (33). A yellow solid formed (78%): mp 88–89 °C; IR (ν CO) 2056, 1923 cm⁻¹; ¹H NMR δ 5.82 (m, 2 H), 5.26 (m, 4 H), 4.38 (d, J = 6.3 Hz, 4 H), 3.46 (s, 4 H); ¹³C NMR δ 221.7, 220.6 (Cr=C), 217.6, 133.2, 119.0 54.5, 48.4. Anal. Calcd for C₁₄H₁₄N₂O₅Cr: C, 49.13; H, 4.12; N, 8.18. Found: C, 49.16; H, 4.11; N, 8.00.

(CO)₅Mo=CN(CH₂CH=CH₂)CH₂CH₂CH₂N(CH₂CH=CH₂) (34). A yellow solid formed (75%): mp 85–87 °C; IR (ν_{CO}) 2064, 1928 cm⁻¹; ¹H NMR δ 5.80 (m, 2 H), 5.25 (m, 4 H), 4.36 (d, J = 6.3 Hz, 4 H), 3.49 (s, 4 H); ¹³C NMR δ 215.9 (Mo=C), 211.9, 206.2, 133.2, 118.8, 54.9, 48.3. Anal. Calcd for C₁₄H₁₄N₂O₅Mo: C, 43.54; H, 3.65; N, 7.25. Found: C, 43.93; H, 3.68; N, 7.20.

(CO)₅W=CN(CH₂CH=CH₂)CH₂CH₂N(CH₂CH=CH₂) (35). A yellow solid formed (83%): mp 107–108 °C; IR (ν_{CO}) 2063, 1924 cm⁻¹; ¹H NMR δ 5.81 (m, 2 H), 5.25 (m, 4 H), 4.36 (m, 4 H), 3.51 (s, 4 H); ¹³C NMR δ 208.0 ($J_{C-W} = 95$ Hz) (W=C), 201.1($J_{C-W} = 129.8$ Hz), 197.9 ($J_{C-W} = 125.3$ Hz), 133.1, 119.0, 55.8, 48.1. Anal. Calcd for C₁₄H₁₄N₂O₅W: C, 35.47; H, 2.98; N, 5.91. Found: C, 35.42; H, 2.95; N, 5.84.

(CO)₄Cr=CN(CH₂CH=CH₂)CH₂CH₂N(CH₂CH=CH₂) (36). Complex 33 (0.3 g, 0.88 mmol) was heated at 90 °C under vacuum, and the desired product was sublimed and deposited as a yellow solid (76%): mp 84–85 °C; IR (ν_{CO}) 2011, 1910, 1865 cm⁻¹; ¹H NMR δ 5.77 (m, 1 H, -CH₂CH=CH₂), 5.19 (m, 2 H, -CH₂CH=CH₂), 4.71 (m, 1 H, coord-CH₂CH=CH₂), 4.14 (dd, J= 15.4, 5.7 Hz, 1 H, coord-CH₂CH=CHH), 3.95 (dd, J= 15.4, 6.4 Hz, 1 H, coord-CH₂CH=CHH), 3.68 (m, 2 H), 3.35 (m, 4 H), 3.19 (d, J= 9 Hz, 1 H), 3.06 (d, J= 13.2 Hz, 1 H); ¹³C NMR δ 234.6, 229.5, 227.0, 225.9, 224.0 (Cr=C), 133.0 (-CH₂CH=CH₂), 118.3 (-CH₂CH=CH₂), 79.7 (coord-CH₂CH=CH₂), 63.6 (coord-CH₂CH=CH₂), 52.9, 50.1, 49.8, 48.2. Anal. Calcd for C₁₃H₁₄N₂O₄Cr: C, 49.69; H, 4.49; N, 8.91. Found: C, 49.31; H, 4.47; N, 8.71.

(CO)₄Mo=CN(CH₂CH=CH₂)CH₂CH₂N(CH₂CH=CH₂) (37). Complex 34 (0.3 g, 0.78 mmol) was heated at 100 °C under vacuum, and the desired complex 37 was sublimed and deposited as a yellow solid (85%): mp 72–73 °C [lit.¹⁷ mp 67–68 °C]; IR (ν _{CO}) 2023, 1920, 1865 cm⁻¹; ¹H NMR δ 5.77 (m, 1 H, -CH₂CH=CH₂), 5.21 (m, 2 H, coord-CH₂CH=CH₂), 5.00 (m,1 H, coord-CH₂CH=CH₂), 4.07 (m, 2 H, -CH₂CH=CH₂), 3.50 (m, 8 H); ¹³C NMR δ 223.7, 222.3, 216.2, 212.7, 212.4, 133.0 (-CH₂CH=CH₂), 118.2 (-CH₂CH=CH₂), 83.4 (coord-CH₂CH=CH₂), 65.8 (CH₂CH=CH₂), 53.7, 51.1, 49.2, 48.8.

(CO)₄W=CN(CH₂CH=CH₂)CH₂CH₂N(CH₂CH=CH₂) (38). Complex 35 was heated at 110 °C under vacuum to provide the desired complex **38** sublimed as a yellow solid (88%): mp 87–88 °C; IR ($\nu_{\rm CO}$) 2022, 1918, 1863 cm⁻¹; ¹H NMR δ 5.75 (m, 1 H, -CH₂CH=CH₂), 5.20 (m, 1H, -CH₂CH=CH₂), 4.66 (m, 1 H, coord-CH₂CH=CH₂), 3.99 (m, 3 H), 3.73 (dd, J=12.0, 4.6 Hz, 1 H, coord-CH₂CH=CHH), 3.42 (m, 4 H), 3.17 (m, 2 H); ¹³C NMR δ 216.7 ($J_{\rm C-W}=91.4$ Hz), 215.5 ($J_{\rm C-W}=153.1$ Hz), 208.3 ($J_{\rm C-W}=139.4$ Hz), 204.4 ($J_{\rm C-W}=119.9$ Hz), 203.8 ($J_{\rm C-W}=119.6$ Hz), 132.8, 118.3, 73.5, 56.1, 54.0, 50.9, 49.2, 48.6. Anal. Calcd for C₁₃H₁₄N₂O₄W: C, 35.00; H, 3.16; N, 6.28. Found: C, 35.01; H, 3.19; N, 6.29.

(CO)₄W=CN(CH₂CH₃)CH₂CH₂N(CH₂CH=CH₂) (39). Complex 32 (1.0 g, 2.16 mmol) was placed in a subliming tube. The apparatus was evacuated and heat to 120 °C. The desired complex sublimed as a yellow solid (91%): mp 106–107 °C; IR (ν_{CO}) 2021, 1919, 1862 cm⁻¹; ¹H NMR δ 4.67 (m, 1 H), 3.91 (dd, J=12.1, 1.0 Hz, 1 H), 3.70 (dd, J=12.1, 4.6 Hz, 1 H), 3.45 (m, 6 H), 3.20 (m, 2 H), 1.14 (t, J=7.2 Hz, 3 H); ¹³C NMR δ 216.0 ($J_{C-W}=91.3$ Hz) (W=C), 215.7 ($J_{C-W}=153.6$ Hz), 208.5 ($J_{C-W}=139.8$ Hz), 204.6 ($J_{C-W}=119.3$ Hz), 203.9 ($J_{C-W}=119.9$ Hz), 73.6, 56.1, 50.8, 48.9, 48.6, 46.1, 13.4. Anal. Calcd for C₁₂H₁₄N₂O₄W: C, 33.20; H, 3.25; N, 6.45. Found: C, 33.22; H, 3.07; N, 6.65.

Br(CO)₄**Re=CNHCH**₂**CH**₂**NH (41).** A mixture of ReBr(CO)₅ (300 mg, 0.74 mmol) and **9** (237 mg, 0.74 mmol) in THF was stirred at 25 °C for 8 h. After removal of solvents, the residue was chromatographed on silica gel with dichloromethane as the eluent. The eluate was concentrated to give **41** as a white solid (87%): mp 131–134 °C (dec); IR (ν_{CO}) 2105, 2003, 1916 cm⁻¹; ¹H NMR δ 6.86 (s, 2 H), 3.72 (s, 4 H); ¹³C NMR δ 192.0 (Re=C), 186.7, 185.0, 45.3. Anal. Calcd for C₇H₆BrO₄N₂Re: C, 18.76; H, 1.35; N, 6.25. Found: C, 18.75; H, 1.32; N, 6.31.

fac-Br(CO)₃**Re[=CNHCH**₂**CH**₂**NH**]₂ **(42).** A mixture of ReBr(CO)₅ (300 mg, 0.74 mmol) and **9** (474 mg, 1.48 mmol) in

THF (10 mL) was stirred at 25 °C for 24 h. After concentration of the reaction mixture, the residue was chromatographed on silica gel with dichloromethane as the eluent. The eluate was concentrated to give **42** as a white solid (57%), which was recrystallized from dichloromethane and hexane to give **42** as a clear, colorless crystalline solid: mp 133–137 °C (dec); IR ($\nu_{\rm CO}$) 2016, 1920, 1852 cm⁻¹; ¹H NMR δ 6.67 (s, 4 H), 3.63 (s, 8 H); ¹³C NMR δ 202.7, 194.9, 193.9 (Re=C), 45.2. Anal. Calcd for C₉H₁₂BrO₃N₄Re: C, 22.05; H, 2.47; N, 11.43. Found: C, 22.05; H, 2.44; N, 11.27.

Crystallography. Single crystals suitable for X-ray analysis of complex **18** and **42** were obtained by slow evaporation of a solution under air. Cell parameters were determined on a CAD-4 diffractometer by a least-squares treatment. Atomic scattering factors were taken from ref 19. Calculations were performed by using the NRCC SDP VAX package.²⁰ The crystal data of **18** and **42** are listed in Table 3, and their non-hydrogen atomic coordinates are listed in Tables 4 and 5, respectively. Other crystallographic data are collected as Supporting Information.

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Supporting Information Available: Tables giving anisotropic thermal parameters and all bond distances and angles for **18** and **42** (4 pages). Ordering information is given on any current masthead page.

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⁽¹⁹⁾ International Tables for X-ray Crystallography; Kynoch Press: Birmingham, U.K., 1974; Vol. VI. (20) Gabe, E. J.; Lee, F. L. Acta Crystallogr. **1981**, A37, S339.