# Synthesis of Cyclic Diamino-Substituted Metal Carbene Complexes

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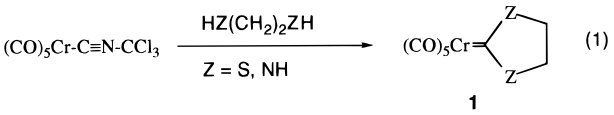
A series of heterocyclic metal carbene complexes were prepared by the deoxygenation reaction of $M(CO)_6$ (M = Cr, Mo, W) with $RNH(CH_2)_nN{=}PPh_3$ (R = H, Et, Ph; $n$ = 2, 3, 4) to form the corresponding isocyanide complex, which subsequently underwent intramolecular cyclization to give $(CO)_5M{=}\overline{CN(R)(CH_2)_n}NH$ in good yields. None of the carbene complex reacted further with amine−phosphinimine $RNH(CH_2)_nN{=}PPh_3$ 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 $\pi$-coordinated complex. Unlike the group VI metal carbonyl complexes, treatment of $ReBr(CO)_5$ with 2 molar equiv of $Ph_3P{=}N(CH_2)_2NH_2$ provided a bis(carbene) complex *fac*-$(CO)_3BrRe(=\overline{CNHCH_2CH_2NH})_2$. All complexes are characterized by both spectral and elemental analyses. Complexes $(CO)_5Mo{=}\overline{CNHCH_2CH_2CH_2NH}$ (**18**) and *fac*-$(CO)_3BrRe(=\overline{CNHCH_2CH_2NH})_2$ (**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 carbonyl−isocyanide complexes toward nucleophiles has not been well explored. It was reported by Fehlhammer and coworkers that $(CO)_5CrCNCCl_3$ reacted with dithiols or diamines to yield the heterocyclic electron-rich carbene complex **1**.[6] It is also known that the stable amino-substituted metal carbene species **1** (Z = NR) can be obtained by oxidative addition of tetraamino-substituted olefins or related species to metal carbonyl complexes.[12]




(1)

**1**

Recently, we reported that phosphinimine−phosphine $Ph_3P{=}N(CH_2)_3PPh_2$ (**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.

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

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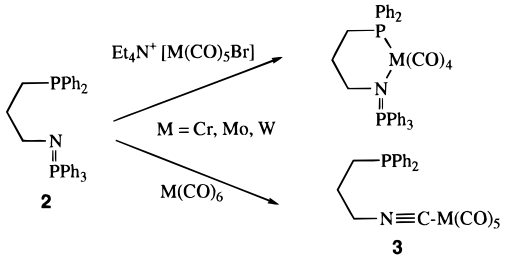
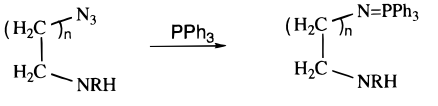
**Scheme 1**




2 3

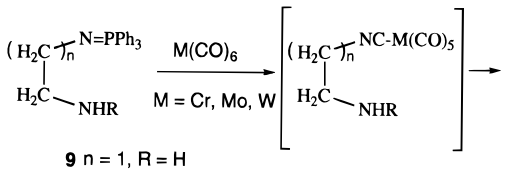
**Scheme 2**



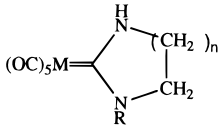

**4** R = H, n = 1
**5** R = H, n = 2
**6** R = H n = 3
**7** R = Et, n = 1
**8** R = Ph, n = 1

**9** R = H, n = 1
**10** R = H, n = 2
**11** R = H, n = 3
**12** R = Et, n = 1
**13** R = Ph, n = 1

**Scheme 3**




**9** n = 1, R = H
**10** n = 2, R = H
**11** n = 3, R = H
**12** n = 1, R = Et
**13** n = 1, R = Ph



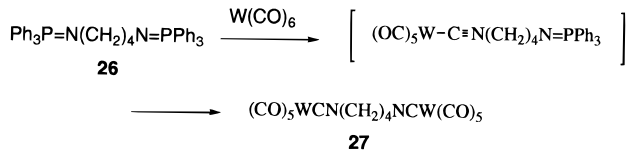

**14** M = Cr, R = H, n = 1
**15** M = Mo, R = H, n = 1
**16** M = W, R = H, n = 1
**17** M = Cr, R = H, n = 2
**18** M = Mo, R = H, n = 2
**19** M = W, R = H, n = 2
**20** M = W, R = H, n = 3
**21** M = Cr, R = Et, n = 1
**22** M = Mo, R = Et, n = 1
**23** M = W, R = Et, n = 1
**24** M = W, R = Ph, n = 1

## Results and Discussion

**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 $^{31}P$ NMR shifts for phosphinimines were in the range of 10−15 ppm (relative to 85% $H_3PO_4$) 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 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 $(CO)_5WCN(CH_2)_4NH_2$ (**25**) exclusively, which was isolated and characterized. This outcome is quite similar to the species $(CO)_5CrCN(CH_2)_4NH_2$ obtained from the reaction of $(CO)_5CrCNCCl_3$ with $NH_2(CH_2)_4NH_2$ 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.

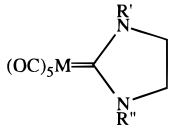
**Scheme 4**



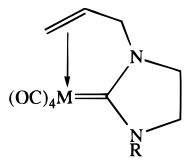

**26** **27**

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 $\pi$-bond coordinated species **36**−**39**. The




**28** M = Cr, R' = Et R" = Et
**29** M = Mo, R' = Et R" = Et
**30** M = W, R' = Et R" = Et
**31** M = W, R' = Et R" = propargyl
**32** M = W, R' = Et R" = allyl
**33** M = Cr, R' = allyl R" = allyl
**34** M = Mo, R' = allyl R" = allyl
**35** M = W, R' = allyl R" = allyl

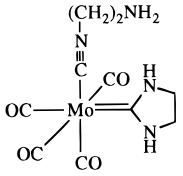



**36** M = Cr, R = allyl
**37** M = Mo, R = allyl
**38** M = W, R = ally
**39** M = W, R = Et

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 $\pi$-bond coordinated species was not formed in **31**.

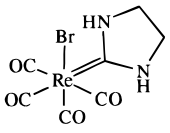
**Bis(carbene) Complexes.** Attempts to prepare the bis(carbene) species were unsuccessful. No reaction was observed when equal molar amounts of **18** and **9** were heated in refluxing THF; neither were the chromium and tungsten analogues formed. As discussed earlier, the formation of the carbene species 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**.



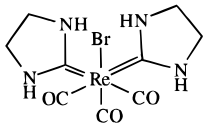

**40**

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 $\pi$-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




**41**




**42**

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 $^{13}C$ 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

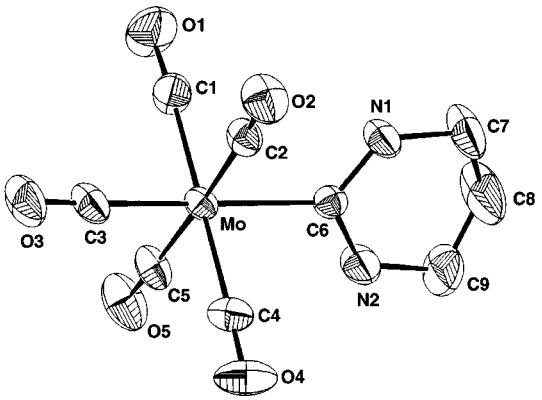



**Figure 1.** ORTEP plot of molybdenum carbene complex **18**.

**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°; N(1)-C(6)-N(2)-C(9) 1.5°], 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)$SiPh_3$ [2.15(2) Å][14] indicating that the metal−carbon bond had more single-bond characteristics. [The distance of Mo−C in $Cp_2Mo(CO)CH_3$ 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)$SiPh_3$.[14a,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) Å]

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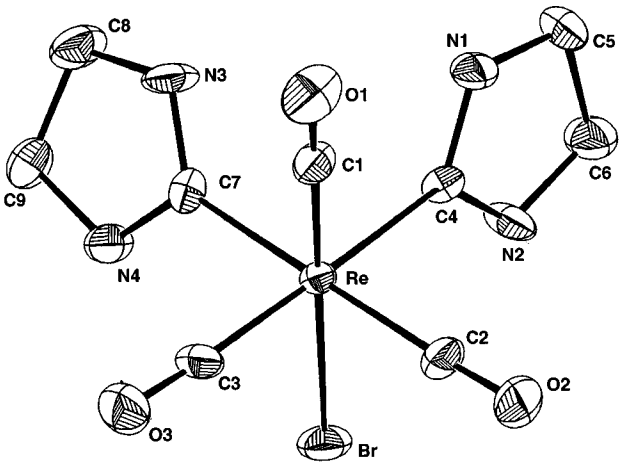


**Figure 2.** ORTEP plot of rhenium bis(carbene) complex **42**.

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

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

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 $CDCl_3$ 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 ($\delta$) 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 $CaH_2$ and then distilled under nitrogen. Other chemicals and solvents were used from commercial sources without further purification. Compounds **4**−**6** were prepared by the method previously reported.[16a]

***N*-(2-Azidoethyl)ethylamine (7).** A solution of $BrCH_2CH_2NHEt\cdot HBr$[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 × 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 $\delta$ 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 $\delta$ 51.5, 48.2, 43.7, 15.2; HRMS calcd for $C_4H_{10}N_4$ *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 $Br(CH_2)_2NHPh\cdot HBr$.[16c] A colorless liquid (82%) forms: IR (neat) $\nu(N_3)$ 2101 $cm^{-1}$; $^1H$ NMR $\delta$ 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); $^{13}C$ NMR $\delta$ 147.1, 129.3, 117.9, 112.9, 50.4, 42.9. HRMS calcd for $C_8H_{10}N_4$ *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.

**$Ph_3P{=}N(CH_2)_2NH_2$ (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 × 2). The desired product was obtained as a white solid (7.30 g, 98%): mp 103−104 °C; $^1H$ NMR $\delta$ 7.75−7.20 (m, 15 H), 3.13 (dt, $^3J_{P-H}$ = 16.5 Hz, $J$ = 6.1 Hz, 2 H), 2.75 (dt, $^3J_{P-H}$ = 1.1 Hz, $J$ = 6.1 Hz, 2 H), 1.85 (br, 2 H); $^{13}C$ NMR $\delta$ (aliphatic) 48.5 (d, $J_{P-C}$ = 5 Hz), 46.4 (d, $J_{P-C}$ = 19 Hz); $^{31}P$ NMR $\delta$ 13.4; HRMS calcd for *m/e* $C_{20}H_{21}N_2P$ 320.1442, found *m/e* 320.1439.

**$Ph_3P{=}N(CH_2)_3NH_2$ (10)**: Viscous liquid; $^1H$ NMR $\delta$ 7.65−7.24 (m, 15 H), 3.12 (dt, $^3J_{P-H}$ = 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); $^{13}C$ NMR $\delta$ (aliphatic) 42.9(d, $J_{P-C}$ = 6.5 Hz), 40.6, 39.0 (d, $J_{P-C}$ = 17 Hz); $^{31}P$ NMR $\delta$ 11.7; HRMS calcd for $C_{21}H_{23}N_2P$ *m/e* 334.1599, found *m/e* 334.1578.

**$Ph_3P{=}N(CH_2)_4NH_2$ (11)**: Viscous liquid; $^1H$ NMR $\delta$ 7.66−7.24 (m, 15 H), 3.06 (dt, $^3J_{P-H}$ = 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, −N*H*); $^{13}C$ NMR $\delta$ (aliphatic) 45.3 (d, $J_{P-C}$ = 4.8 Hz), 42.2, 32.8 (d, $J_{P-C}$ = 17.3 Hz), 31.7; $^{31}P$ NMR $\delta$ 11.6; HRMS calcd for *m/e* $C_{22}H_{25}N_2P$ 348.1755, found *m/e* 348.1749.

**$Ph_3P{=}N(CH_2)_2NH(CH_2CH_3)$ (12)**: Viscous liquid; $^1H$ NMR $\delta$ 7.70−7.25 (m, 15 H), 3.22 (dt, $^3J_{P-H}$ = 15.4, $J$ = 6.0 Hz, 2 H), 2.75 (dt, $^3J_{P-H}$ = 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); $^{13}C$ NMR $\delta$ (aliphatic) 53.9 (d, $J_{P-C}$ = 20 Hz), 44.7 (d, $J_{P-C}$ = 5.1 Hz), 43.9, 15.4; $^{31}P$ NMR $\delta$ 12.6; HRMS calcd for $C_{22}H_{25}N_2P$ *m/e* 348.1755, found *m/e* 348.1749.

**$Ph_3P{=}N(CH_2)_2NHPh$ (13)**: Viscous liquid; $^1H$ NMR $\delta$ 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); $^{13}C$ NMR $\delta$ (aliphatic) 47.5 (d, $J_{P-C}$ = 17.5 Hz), 42.9 (d, $J_{P-C}$ = 4.7 Hz); $^{31}P$ NMR $\delta$ 14.4; HRMS calcd for $C_{26}H_{25}N_2P$ *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.

**$(CO)_5Cr{=}\overline{CNHCH_2CH_2NH}$ (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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(17) Chamizo, J. A.; Hitchcock, P. B.; Jasim, H. A.; Lappert, M. F. *J. Organomet. Chem.* **1993**, *451*, 89.

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 ($\nu_{CO}$) 2058, 1924 cm$^{-1}$; $^1$H NMR $\delta$ 6.03 (br, 2 H), 3.62 (s, 4 H); $^{13}$C NMR $\delta$ 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.

**$(CO)_5Mo$=CNHCH$_2$CH$_2$NH (15).** A light yellow solid formed (70%): mp 109−110 °C; IR ($\nu_{CO}$) 2064, 1928 cm$^{-1}$; $^1$H NMR $\delta$ 6.02 (br, 2 H), 3.59 (s, 4 H); $^{13}$C NMR $\delta$ 213.5 (Mo=*C*), 211.9, 206.6, 44.6. Anal. Calcd for $C_8H_6N_2O_5CMo$: C, 31.39; H, 1.98; N, 9.15. Found: C, 31.20; H, 2.01; N, 9.11.

**$(CO)_5W$=CNHCH$_2$CH$_2$NH (16).** A light yellow solid formed (87%): mp 129−130 °C; IR ($\nu_{CO}$) 2064, 1921 cm$^{-1}$; $^1$H NMR $\delta$ 5.97 (br, 2 H), 3.65 (s, 4 H); $^{13}$C NMR $\delta$ 204.0 (W=*C*), 201.8, 198.0, 45.1. Anal. Calcd for $C_8H_6N_2O_5CW$: C, 24.39; H, 1.53; N, 7.11. Found: C, 24.31; H, 1.42; N, 7.09.

**$(CO)_5Cr$=CNH(CH$_2$)$_3$NH (17).** A colorless solid formed (66%): mp 142−143 °C [lit.[6a] mp 145 °C]; IR ($\nu_{CO}$) 2055, 1921 cm$^{-1}$; $^1$H NMR $\delta$ 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); $^{13}$C NMR $\delta$ 221.7, 218.1, 214.8 (Cr=*C*), 40.7, 19.7. Anal. Calcd for $C_9H_8N_2O_5Cr$: C, 39.14; H, 2.92; N, 10.14. Found: C, 38.92; H, 2.82, N, 10.07.

**$(CO)_5Mo$=CNH(CH$_2$)$_3$NH (18).** A light yellow solid formed (64%): mp 139−141 °C; IR ($\nu_{CO}$) 2063, 1924 cm$^{-1}$; $^1$H NMR $\delta$ 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); $^{13}$C NMR $\delta$ 212.1, 208.9 (Mo=*C*), 206.9, 40.2, 19.7. Anal. Calcd for $C_9H_8N_2O_5Mo$: C, 33.77; H, 2.52; N, 8.75. Found: C, 33.78; H, 2.49; N, 8.51.

**$(CO)_5W$=CNH(CH$_2$)$_3$NH (19).** A light yellow solid formed (84%): mp 164−165 °C; IR ($\nu_{CO}$) 2062, 1917 cm$^{-1}$; $^1$H NMR $\delta$ 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); $^{13}$C NMR $\delta$ 202.0, 199.2 (W=*C*), 198.9, 40.5, 19.4. Anal. Calcd for $C_9H_8N_2O_5W$: C, 26.49; H, 1.98; N, 6.87. Found: C, 26.38; H, 1.92; N, 6.78.

**$(CO)_5W$=CNH(CH$_2$)$_4$NH (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 ($\nu_{CO}$) 2064, 1918 cm$^{-1}$; $^1$H NMR $\delta$ 6.07 (br, 2 H, N*H*), 3.42 (m, 4 H), 1.94 (m, 4 H); $^{13}$C NMR $\delta$ 202.0, 199.0, 194.2 (W=*C*), 46.4, 26.7. Anal. Calcd for $C_{10}H_{10}N_2O_5W$: C, 28.46; H, 2.39; N, 6.64. Found: C, 28.53; H, 2.27; N, 6.55.

**$(CO)_5Cr$=CN(CH$_2$CH$_3$)CH$_2$CH$_2$NH (21).** A yellow crystalline solid formed (55%): mp 75−76 °C; IR ($\nu_{CO}$) 2056, 1923 cm$^{-1}$; $^1$H NMR $\delta$ 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); $^{13}$C NMR $\delta$ 221.8, 219.2 (Cr=*C*), 218.0, 47.8, 45.1, 44.5, 13.4. Anal. Calcd for $C_{10}H_{10}N_2O_5Cr$: C, 41.39; H, 3.47; N, 9.65. Found: C, 41.37; H, 3.51; N, 9.36.

**$(CO)_5Mo$=CN(CH$_2$CH$_3$)CH$_2$CH$_2$NH (22).** A yellow solid formed (64%): mp 80−81 °C; IR ($\nu_{CO}$) 2064, 1927 cm$^{-1}$; $^1$H NMR $\delta$ 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); $^{13}$C NMR $\delta$ 213.7 (Mo=*C*), 212.0, 206.7, 47.1, 45.8, 44.9, 13.5. Anal. Calcd for $C_{10}H_{10}N_2O_5Mo$: C, 35.95; H, 3.02; N, 8.38. Found: C, 36.17; H, 2.90; N, 8.32.

**$(CO)_5W$=CN(CH$_2$CH$_3$)CH$_2$CH$_2$NH (23).** A yellow solid formed (96%): mp 96−97 °C; IR ($\nu_{CO}$) 2063, 1930 cm$^{-1}$; $^1$H NMR $\delta$ 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); $^{13}$C NMR $\delta$ 204.7 ($J_{P-W}$ = 91.4 Hz) (W=*C*), 201.6 ($J_{P-W}$ = 131.4 Hz), 198.1 ($J_{P-W}$ = 125.5 Hz), 47.1, 46.6, 45.1, 13.5. Anal. Calcd for $C_{10}H_{10}N_2O_5W$: C, 28.46; H, 2.39; N, 6.64. Found: C, 27.95; H, 2.28; N, 6.50.

**$(CO)_5W$=CN(Ph)CH$_2$CH$_2$NH (24).** A light yellow solid formed (78%): mp 95−96 °C; IR ($\nu_{CO}$) 2064, 1926 cm$^{-1}$; $^1$H NMR $\delta$ 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 $\delta$ 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.

**$(CO)_5WCN(CH_2)_4NH_2$ (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 ($\nu_{NC}$) 2177 cm$^{-1}$, ($\nu_{CO}$) 2068, 1945 cm$^{-1}$; $^1$H NMR $\delta$ 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); $^{13}$C NMR $\delta$ 196.3, 194.3, 142.1 (*C*N−), 44.1, 41.0, 30.1, 26.6. Anal. Calcd for $C_{10}H_{10}N_2O_5W$: C, 28.46; H, 2.39; N, 6.64. Found: C, 28.30; H, 2.59; N, 6.47.

**$Ph_3P=N(CH_2)_4N=PPh_3$ (26).** The preparation of **26** is similar to the method described for **9** except $N_3(CH_2)_4N_3$[18] was used. A white solid formed (99%): mp 112−113 °C (dec); $^1$H NMR $\delta$ 7.64−7.26 (m, 30 H), 3.05 (m, 4 H), 1.58 (m, 4 H); $^{13}$C NMR $\delta$ (aliphatic) 45.70 (d, $J_{P-C}$ = 5.3 Hz), 33.63 (d, $J_{P-C}$ = 16.7 Hz); $^{31}$P NMR $\delta$ 10.64.

**$(CO)_5WCN(CH_2)_4NCW(CO)_5$ (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 ($\nu_{CN}$) 2171 cm$^{-1}$, ($\nu_{CO}$) 2066, 1948 cm$^{-1}$; $^1$H NMR $\delta$ 3.78 (m, 4 H), 1.94 (m, 4 H); $^{13}$C NMR $\delta$ 195.9, 194.1, 144.6 (−N*C*), 43.4, 26.3. Anal. Calcd for $C_{16}H_8N_2O_{10}W_2$: 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$_2$CH$_3$)CH$_2$CH$_2$N(CH$_2$CH$_3$) (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($\nu_{CO}$) 2054, 1929 cm$^{-1}$; $^1$H NMR $\delta$ 3.82 (q, $J$ = 7.1 Hz, 4 H), 3.51 (s, 4 H), 1.24 (t, $J$ = 7.1 Hz, 6 H); $^{13}$C NMR $\delta$ 222.1, 219.2 (Cr=*C*), 217.9, 47.7, 46.0, 13.6. Anal. Calcd for $C_{12}H_{14}N_2O_5Cr$: C, 45.29; H, 4.43; N, 8.80. Found: C, 45.15; H, 4.32; N, 8.75.

**$(CO)_5Mo$=CN(CH$_2$CH$_3$)CH$_2$CH$_2$N(CH$_2$CH$_3$) (29).** A light yellow solid formed (73%): mp 92−93 °C [lit.[12b] mp 93 °C]; IR ($\nu_{CO}$) 2063, 1928 cm$^{-1}$; $^1$H NMR $\delta$ 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 $\delta$ 214.1 (Mo=*C*), 212.2, 206.5, 47.6, 46.4, 13.5. Anal. Calcd for $C_{12}H_{14}N_2O_5Mo$: C, 39.79; H, 3.90; N, 7.73. Found: C, 39.48; H, 3.94; N, 7.88.

**$(CO)_5W$=CN(CH$_2$CH$_3$)CH$_2$CH$_2$N(CH$_2$CH$_3$) (30).** A light yellow solid (87%): mp 99−100 °C [lit.[12c] mp 102 °C]; IR ($\nu_{CO}$) 2062, 1919 cm$^{-1}$; $^1$H NMR $\delta$ 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 | $C_9H_8N_2O_5Mo$ | $C_9H_{12}BrN_4O_3Re$ |
| 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) |
| 2*θ* range, deg | 22.60−31.72 | 15.72−37.00 |
| *F*(000) | 632 | 456 |
| Z | 4 | 2 |
| $D_{calcd}$, g cm$^{-3}$ | 1.679 | 2.354 |
| *μ*, cm$^{-1}$ | 10.198 | 117.674 |
| scan width | *ω*−2*θ* | *ω*−2*θ* |
| radiation | Mo Kα | Mo Kα |
| cryst dimens, mm | 0.30 × 0.35 × 0.50 | 0.20 × 0.20 × 0.50 |
| scan width | 2(1.00 + 0.35 tan *θ*) | 2(0.70 + 0.35 tan *θ*) |
| transm range | 0.939; 1.00 | 0.787; 1.00 |
| 2*θ* max, deg | 50.0 | 45.0 |
| no. of unique reflns | 1316 | 1804 |
| no. of reflns obsd[a] | 1209 | 1664 |
| computation | NRCSDP-VAX | NRCSDP-VAX |
| soln method | heavy atom | heavy atom |
| no. of params | 155 | 164 |
| R | 0.025 | 0.035 |
| $R_w$ | 0.027 | 0.055 |
| S | 2.77 | 2.03 |

[a] $I > 2\sigma(I)$. [b] $R = \sum|F_o - F_c|/\sum(F_o)$; $R_w = [\sum w(F_o - F_c)^2/\sum(wF_o)^2]^{1/2}$; $S = [\sum w(F_o - F_c)^2/(\text{no. of reflns} - \text{no. of params})]$.

**Table 4. Atomic Coordinates and Isothermal Parameters (Å$^2$) for 18**

| | *x* | *y* | *z* | $B_{eq}$ |
|---|---|---|---|---|
| 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); $^{13}$C 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($CH_2CH_3$)$CH_2CH_2$N($CH_2CCH$) (31).** A yellow solid formed (86%): mp 93−94 °C; IR ($\nu_{CO}$) 2064, 1920 cm$^{-1}$; $^1$H 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); $^{13}$C 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 $C_{13}H_{12}N_2O_5W$: C, 33.94; H, 2.63; N, 6.09. Found: C, 33.85; H, 2.46; N, 6.16.

**$(CO)_5W$=CN($CH_2CH_3$)$CH_2CH_2$N($CH_2C$=$CH_2$) (32).** A yellow solid formed (85%): IR ($\nu_{CO}$) 2063, 1920 cm$^{-1}$; $^1$H 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); $^{13}$C NMR *δ* 206.7 ($J_{C-W}$ = 95 Hz) (W=*C*), 201.4 ($J_{C-W}$ = 129.8 Hz), 197.9 ($J_{C-W}$ = 125.7 Hz), 133.1, 118.9, 55.6, 47.9, 47.5, 47.4, 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.

**Table 5. Atomic Coordinates and Isothermal Parameters (Å$^2$) for 42**

| | *x* | *y* | *z* | $B_{eq}$ |
|---|---|---|---|---|
| Re | 0.24517(10) | 0.19503(9) | 0.23993(5) | 2.52(3) |
| 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) |

**$(CO)_5Cr$=CN($CH_2CH$=$CH_2$)$CH_2CH_2$N($CH_2CH$=$CH_2$) (33).** A yellow solid formed (78%): mp 88−89 °C; IR ($\nu_{CO}$) 2056, 1923 cm$^{-1}$; $^1$H 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); $^{13}$C NMR *δ* 221.7, 220.6 (Cr=*C*), 217.6, 133.2, 119.0 54.5, 48.4. Anal. Calcd for $C_{14}H_{14}N_2O_5Cr$: C, 49.13; H, 4.12; N, 8.18. Found: C, 49.16; H, 4.11; N, 8.00.

**$(CO)_5Mo$=CN($CH_2CH$=$CH_2$)$CH_2CH_2$N($CH_2CH$=$CH_2$) (34).** A yellow solid formed (75%): mp 85−87 °C; IR ($\nu_{CO}$) 2064, 1928 cm$^{-1}$; $^1$H 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); $^{13}$C NMR *δ* 215.9 (Mo=*C*), 211.9, 206.2, 133.2, 118.8, 54.9, 48.3. Anal. Calcd for $C_{14}H_{14}N_2O_5Mo$: C, 43.54; H, 3.65; N, 7.25. Found: C, 43.93; H, 3.68; N, 7.20.

**$(CO)_5W$=CN($CH_2CH$=$CH_2$)$CH_2CH_2$N($CH_2CH$=$CH_2$) (35).** A yellow solid formed (83%): mp 107−108 °C; IR ($\nu_{CO}$) 2063, 1924 cm$^{-1}$; $^1$H NMR *δ* 5.81 (m, 2 H), 5.25 (m, 4 H), 4.36 (m, 4 H), 3.51 (s, 4 H); $^{13}$C 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 $C_{14}H_{14}N_2O_5W$: C, 35.47; H, 2.98; N, 5.91. Found: C, 35.42; H, 2.95; N, 5.84.

**$(CO)_4Cr$=CN($CH_2CH$=$CH_2$)$CH_2CH_2$N($CH_2CH$=$CH_2$) (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 ($\nu_{CO}$) 2011, 1910, 1865 cm$^{-1}$; $^1$H NMR *δ* 5.77 (m, 1 H, $-CH_2CH$=$CH_2$), 5.19 (m, 2 H, $-CH_2CH$=$CH_2$), 4.71 (m, 1 H, coord-$CH_2CH$=$CH_2$), 4.14 (dd, *J* = 15.4, 5.7 Hz, 1 H, coord-$CH_2CH$=$CH$H), 3.95 (dd, *J* = 15.4, 6.4 Hz, 1 H, coord-$CH_2CH$=$CH$H), 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); $^{13}$C NMR *δ* 234.6, 229.5, 227.0, 225.9, 224.0 (Cr=*C*), 133.0 ($-CH_2CH$=$CH_2$), 118.3 ($-CH_2CH$=$CH_2$), 79.7 (coord-$CH_2CH$=$CH_2$), 63.6 (coord-$CH_2CH$=$CH_2$), 52.9, 50.1, 49.8, 48.2. Anal. Calcd for $C_{13}H_{14}N_2O_4Cr$: C, 49.69; H, 4.49; N, 8.91. Found: C, 49.31; H, 4.47; N, 8.71.

**$(CO)_4Mo$=CN($CH_2CH$=$CH_2$)$CH_2CH_2$N($CH_2CH$=$CH_2$) (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 ($\nu_{CO}$) 2023, 1920, 1865 cm$^{-1}$; $^1$H NMR *δ* 5.77 (m, 1 H, $-CH_2CH$=$CH_2$), 5.21 (m, 2 H, coord-$CH_2CH$=$CH_2$), 5.00 (m,1 H, coord-$CH_2CH$=$CH_2$), 4.07 (m, 2 H, $-CH_2CH$=$CH_2$), 3.50 (m, 8 H); $^{13}$C NMR *δ* 223.7, 222.3, 216.2, 212.7, 212.4, 133.0 ($-CH_2CH$=$CH_2$), 118.2 ($-CH_2CH$=$CH_2$), 83.4 (coord-$CH_2CH$=$CH_2$), 65.8 ($CH_2CH$=$CH_2$), 53.7, 51.1, 49.2, 48.8.

**$(CO)_4W$=CN($CH_2CH$=$CH_2$)$CH_2CH_2$N($CH_2CH$=$CH_2$) (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 ($\nu_{CO}$) 2022, 1918, 1863 $cm^{-1}$; $^1H$ NMR $\delta$ 5.75 (m, 1 H, $-CH_2CH{=}CH_2$), 5.20 (m, 1H, $-CH_2CH{=}CH_2$), 4.66 (m, 1 H, coord-$CH_2CH{=}CH_2$), 3.99 (m, 3 H), 3.73 (dd, $J$ = 12.0, 4.6 Hz, 1 H, coord-$CH_2CH{=}CHH$), 3.42 (m, 4 H), 3.17 (m, 2 H); $^{13}C$ NMR $\delta$ 216.7 ($J_{C-W}$ = 91.4 Hz), 215.5 ($J_{C-W}$ = 153.1 Hz), 208.3 ($J_{C-W}$ = 139.4 Hz), 204.4 ($J_{C-W}$ = 119.9 Hz), 203.8 ($J_{C-W}$ = 119.6 Hz), 132.8, 118.3, 73.5, 56.1, 54.0, 50.9, 49.2, 48.6. Anal. Calcd for $C_{13}H_{14}N_2O_4W$: C, 35.00; H, 3.16; N, 6.28. Found: C, 35.01; H, 3.19; N, 6.29.

**$(CO)_4W{=}C\overline{N(CH_2CH_3)CH_2CH_2N(CH_2CH{=}CH_2)}$ (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 ($\nu_{CO}$) 2021, 1919, 1862 $cm^{-1}$; $^1H$ NMR $\delta$ 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); $^{13}C$ NMR $\delta$ 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 $C_{12}H_{14}N_2O_4W$: C, 33.20; H, 3.25; N, 6.45. Found: C, 33.22; H, 3.07; N, 6.65.

**$Br(CO)_4Re{=}\overline{CNHCH_2CH_2NH}$ (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 ($\nu_{CO}$) 2105, 2003, 1916 $cm^{-1}$; $^1H$ NMR $\delta$ 6.86 (s, 2 H), 3.72 (s, 4 H); $^{13}C$ NMR $\delta$ 192.0 (Re=*C*), 186.7, 185.0, 45.3. Anal. Calcd for $C_7H_6BrO_4N_2Re$: C, 18.76; H, 1.35; N, 6.25. Found: C, 18.75; H, 1.32; N, 6.31.

***fac*-$Br(CO)_3Re[{=}\overline{CNHCH_2CH_2NH}]_2$ (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 ($\nu_{CO}$) 2016, 1920, 1852 $cm^{-1}$; $^1H$ NMR $\delta$ 6.67 (s, 4 H), 3.63 (s, 8 H); $^{13}C$ NMR $\delta$ 202.7, 194.9, 193.9 (Re=*C*), 45.2. Anal. Calcd for $C_9H_{12}BrO_3N_4Re$: 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.

OM950735Q

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