Synthesis and Coordination Chemistry of a Novel Phosphinimine Phosphine

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The incorporation of a phosphinimino moiety into phosphine ligands to form a new bidentate $Ph_3P{=}N(CH_2)_3PPh_2$ (**1**) is reported. Compound **1** can act as a σ-N and σ-P donor ligand or react with metal carbonyls to form isocyanide complexes. Complexes of $(CO)_4M$-(**1**-*P*,*N*) [M = Mo (**2**), W (**3**)] were prepared from the reaction of $Et_4N[M(CO)_5Br]$ with **1** in refluxing THF solution, whereas the isocyanide complexes of $(CO)_5MCN(CH_2)_3PPh_2$ [M = Cr (**4**), Mo (**5**), W (6)] are obtained from the reaction of $M(CO)_6$ with **1** at 25 °C. The deoxygenation nature is also shown in the reaction of $CpFe(CO)_2I$, $CpRu(CO)_2I$, $Re(CO)_5Br$, and $Re_2(CO)_{10}$ with **1** to form the corresponding isocyanide complexes [$CpFe(CO)\{CN(CH_2)_3$-PPh_2-*C*,*P*}]I (**7**), $CpRu(CO)I\{CN(CH_2)_3PPh_2$-*C*} (**10**), $BrRe(CO)_{5-n}\{CN(CH_2)_3PPh_2$-*C*$\}_n$ [*n* = 1 (**12**), 2 (**14**)], and $Re_2(CO)_9\{CN(CH_2)_3PPh_2$-*C*} (**15**), respectively. The free phosphine of **10** underwent exchange with one triphenylphosphine ligand in $CpRu(PPh_3)_2Cl$ to yield the binuclear species [$CpRu(PPh_3)Cl\{P(Ph_2)(CH_2)_3NC\}Ru(CO)CpI$] (**11**), whereas intramolecular ligand substitution occurred in both **12** and **15** to give $Br(CO)_3Re\{CN(CH_2)_3PPh_2$-*C*,*P*} (**13**) and $\{\mu$-$CN(CH_2)_3PPh_2\}Re_2(CO)_8$ (**16**). Reaction of $(COD)PdCl_2$ with **1** produced the complex (**1**-*P*,*N*)$PdCl_2$ (**18**), in which **1** acts as a σ-N, σ-P bidentate ligand. X-ray crystal structural analysis of [$CpFe(CO)\{CN(CH_2)_3PPh_2$-*C*,*P*}]$PF_6$ (**7a**) and **18** confirmed the formulation of both complexes. The C≡N bond distance [1.20(3) Å] of **7a** is greater than those in the related iron–isocyanide complexes; the angle C–N–C [141(2)°] deviates from 180°, indicating that the resonance contribution of Fe=C=N– is more important than that of Fe–C≡N–. These observations are consistent with spectral data, the smaller infrared stretching wavenumber (2089 cm^{-1}), and the greater shift (^{13}C NMR δ 183.7 ppm) of the isocyanide moiety of **7**.

Introduction

The nature of the highly polar P–N bond in phosphinimine makes a ligand of this kind versatile in both coordination and organometallic chemistry.[1-14] The nitrogen atom of phosphinimine is able to act as a two-electron donor for complexation with various metal ions[2,3] and as a four-electron donor (bridging mode) in $Mo_2(CO)_6(Ph_3PNH)_3$.[4] Furthermore, phosphinimines can react with metal carbonyl complexes[6] and metal oxides[7] to produce isocyanide and nitrene functions, respectively, by elimination of phosphine oxide.

Incorporation of a phosphinimino moiety with other donor atoms to form a chelate bidentate has been reported for 9,10-$H_2NC_{14}H_8N{=}PPh_3$,[8] *o*-$(HO)C_6H_4N{=}PPh_3$,[9] 8-$(Ph_3P{=}N{-})C_9H_6N$,[10] (η^1-C_5Me_5)$P{=}N(t$-Bu),[11] $Ph_3P{=}NC_6H_4N{=}PPh_3$,[7b,12] $Ph_2P(=NR)CH_2PPh_2(=NR)$,[13] and $PhN{=}P(Ph_2)CH{=}CH(p$-Tol)(NH_2).[14] Among these bidentate ligands, only one phosphine–phosphinimine, $Ph_2PCH_2PPh_2(=NSiMe_3)$, is reported,[15] for which the coordination mode toward metal ions is confined due to the short carbon chain. We recently showed that the phosphinimine function is stable toward the phosphide nucleophile, which allows us to prepare the potential bidentate phosphino–phosphinimine ligands **1**.[16] Analogous to $Ph_2PCH_2PPh_2(=NSiMe_3)$, one expects compound **1** to be able to coordinate in a σ-N and σ-P chelate mode toward metal ions and that compound **1** would react

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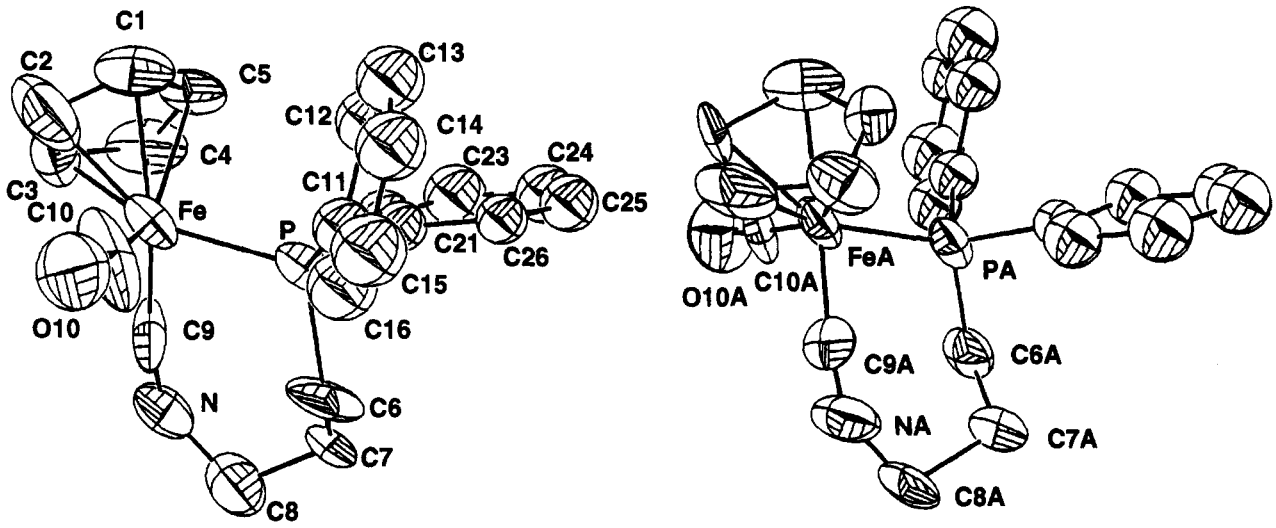
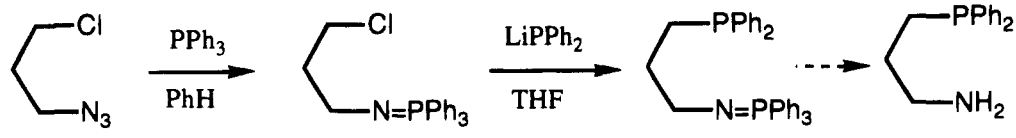


Figure 1. ORTEP view of the cation of complex **7a** showing 50% probability thermal ellipsoids. Two indepent molecules exist in the unit cell.

Scheme 1



1

with a metal–carbonyl ligand to form a new ligand CN-$(CH_2)_3PPh_2$ of bidenate type in either a bridging or a chelating mode. Here we report the results of coordination chemistry of **1** toward various metal complexes.

$$Ph_3P{=}N{-}(CH_2)_3{-}PPh_2$$
1

Results and Discussion

The ligand $Ph_3P{=}N(CH_2)_3PPh_2$ was obtained after isolation of the intermediate in the synthesis of H_2N-$(CH_2)_3PPh_2$ (Scheme 1).[16] This phosphino–phosphinimine **1** is stable in air but sensitive to moisture. The ^{31}P NMR spectrum of the new ligand displays two singlets at −16.0 and 4.3 ppm in benzene-d_6 for diphenylphosphino and iminophosphorane moieties, respectively. The ^{31}P chemical shift corresponding to the moiety of $Ph_3P{=}N-$ is varied from nonpolar solvent to polar solvent. Thus the chemical shift of the phosphinimino moiety is 12.1 ppm in $CDCl_3$, indicating the polar nature of the P—N bond.

Addition of **1** to a stirred tetrahydrofuran solution of $NEt_4[M(CO)_5Br]$ (M = Mo, W) at refluxing temperature results in the formation of chelate complexes $(CO)_4M$-(**1**-*P,N*) [**2**, M = Mo; **3**, M = W]. Both complexes were isolated as solids stable in air and characterized by spectral methods. The carbonyl stretching wavenumbers of the complexes occur in the 2010–1900 cm^{-1} region, which is in accord with a tetracarbonyl species. The ^{31}P NMR spectrum displays two sets of doublets [39.4 (d, J = 14 Hz), 16.3 (d, J = 14 Hz) ppm for **2** and 37.9 (d, J = 18 Hz), 2.67 (dt, J_{P-P} = 18 Hz, J_{P-W} = 224 Hz) ppm for **3**] due to phosphorus atoms of two kinds coupled to each other. Both the coordination chemical shifts and long range phosphorus–phosphorus coulings verify the existence of the $Ph_3P{=}N-$ moiety in the complexes. The infrared spectra of both **2** and **3** exhibit no band that could be assigned to C≡N− modes, in agreement with the structural formulation. Apparently, compound **1** acts as a simple chelate ligand (a σ-N and σ-P chelate mode) in Mo(0) and W(0) complexes.

Table 1. Infrared Absorptions and ^{13}C NMR Chemical Shifts of Isocyanide Complexes[a]

complex	ν_{CN}, cm^{-1}	^{13}C NMR, ppm	ref
4	2173	162.5	this work
5	2173	153.4	this work
6	2175	143.0	this work
7	2089	183.7 (d, J_{P-C} = 35 Hz)	this work
$[CpFe(PPh_3)(CO)(CNCH_3)]BF_4$	2194		20
10	2170	145.1	this work
11	2170	144.9, 144.8[c]	this work
12	2222	129.2	this work
$ReBr(CO)_4(CNPr)$	2221	129.4	21
13	2138	163(d, J_{P-C} = 6.8 Hz)	this work
fac-$Re(CO)_3(CN^tBu)(PPh_2Me)Br$	2186		23
fac-$Re(CO)_3(CN^tBu)(PPh_3)Br$	2181		23
14	2219, 2192	134.3	this work
$ReBr(CO)_3(CNPr)_2$	2219, 2197	134.5	21
15	2187	134.5	this work
$Re_2(CO)_9(CN^tBu)$	2173[d]		22
16	2156[b]	178.9	this work
17	2221	130.7	this work

[a] Recored in CH_2Cl_2 for IR and in $CDCl_3$ for ^{13}C NMR, unless otherwise noted. [b] KBr. [c] Diastereomers. [d] In hexane.

Deoxygenation of the carbonyl group took place in the reaction of **1** with $M(CO)_6$ at room temperature to yield the corresponding isocyanide complex $(CO)_5M[CN(CH_2)_3$-PPh_2-*C*) [**4**, M = Cr; **5**, M = Mo; **6**, M = W]. The structural determination of **4**–**6** was confirmed by infrared and NMR spectra. Infrared spectra of these series complexes exhibit characteristic absorptions at ca. 2174 cm^{-1} for the coordinated isocyanide group and

Table 2. Atomic Parameters and Thermal Parameters of 7a

	x	y	z	B_{eq}, Å^2
Fe	0.8039(4)	0.10504(21)	0.3151(3)	4.74(20)
FeA	−0.2101(4)	0.60450(21)	0.1790(3)	4.93(21)
P	0.9299(8)	0.0482(4)	0.2060(5)	4.5(4)
PA	−0.0815(8)	0.5491(4)	0.2933(5)	4.5(4)
C1	0.693(3)	0.0222(15)	0.3925(16)	5.8(15)
C2	0.644(3)	0.0930(17)	0.4132(22)	9.4(22)
C3	0.764(3)	0.1324(15)	0.4491(18)	6.3(16)
C4	0.891(3)	0.0897(16)	0.4446(17)	6.7(16)
C5	0.8376(25)	0.0201(14)	0.4105(15)	5.0(14)
C6	1.000(3)	0.1108(13)	0.1170(16)	6.4(17)
C7	1.138(3)	0.1578(13)	0.1465(18)	7.1(17)
C8	1.106(3)	0.2374(15)	0.1836(18)	6.6(18)
N	0.9989(22)	0.2295(10)	0.2562(13)	5.6(12)
C9	0.9133(25)	0.1844(14)	0.2854(18)	5.6(15)
C10	0.668(3)	0.1222(15)	0.2373(23)	9.4(21)
O10	0.5616(20)	0.1276(12)	0.1930(13)	9.1(13)
C11	0.818(3)	−0.0158(14)	0.1395(15)	4.9(6)
C12	0.778(3)	−0.0877(15)	0.1793(16)	5.7(7)
C13	0.678(3)	−0.1348(15)	0.1320(16)	5.9(7)
C14	0.622(3)	−0.1131(15)	0.0470(16)	5.9(7)
C15	0.659(3)	−0.0480(16)	0.0074(18)	6.9(8)
C16	0.753(3)	0.0006(15)	0.0554(17)	6.4(7)
C21	1.0888(24)	−0.0072(13)	0.2416(14)	4.1(6)
C22	1.176(3)	0.0137(14)	0.3150(16)	5.5(7)
C23	1.301(3)	−0.0266(15)	0.3377(17)	6.5(7)
C24	1.346(3)	−0.0803(15)	0.2771(16)	5.9(7)
C25	1.265(3)	−0.1006(14)	0.2047(15)	5.3(7)
C26	1.1355(24)	−0.0681(13)	0.1824(14)	3.9(6)
C1A	−0.109(3)	0.5891(15)	0.0512(17)	6.6(16)
C2A	−0.246(4)	0.6364(15)	0.0397(19)	8.5(20)
C3A	−0.364(3)	0.5954(15)	0.0664(19)	7.5(17)
C4A	−0.307(3)	0.5193(15)	0.0988(16)	6.5(16)
C5A	−0.162(3)	0.5223(14)	0.0827(14)	4.5(14)
C6A	−0.009(3)	0.6139(14)	0.3840(16)	5.3(15)
C7A	0.124(3)	0.6643(14)	0.3626(18)	6.1(16)
C8A	0.074(3)	0.7477(14)	0.3228(19)	6.9(18)
NA	−0.029(3)	0.7323(11)	0.2462(13)	7.1(14)
C9A	−0.104(3)	0.6870(14)	0.2157(16)	6.3(16)
C10A	−0.350(3)	0.6229(14)	0.2482(17)	5.2(14)
O10A	−0.4500(20)	0.6329(12)	0.2949(12)	8.7(13)
C11A	−0.1901(25)	0.4821(13)	0.3532(15)	4.6(6)
C12A	−0.252(3)	0.4972(15)	0.4341(16)	5.6(7)
C13A	−0.344(3)	0.4453(17)	0.4784(19)	8.1(8)
C14A	−0.369(3)	0.3783(16)	0.4340(18)	7.1(8)
C15A	−0.319(3)	0.3588(16)	0.3554(18)	7.6(8)
C16A	−0.222(3)	0.4086(14)	0.3099(16)	5.6(7)
C21A	0.0803(24)	0.4988(13)	0.2652(14)	3.9(6)
C22A	0.129(3)	0.4378(15)	0.3219(16)	5.7(7)
C23A	0.268(3)	0.4053(15)	0.3038(16)	5.8(7)
C24A	0.344(3)	0.4237(16)	0.2312(17)	6.6 (7)
C25A	0.297(3)	0.4861(16)	0.1718(17)	6.7(7)
C26A	0.165(3)	0.5195(15)	0.1943(16)	5.5(7)
P1	0.2762(10)	0.7122(5)	−0.0048(6)	7.3(5)
F1	0.373(3)	0.7305(10)	0.0772(15)	15.7(16)
F2	0.189(3)	0.6917(14)	−0.0872(16)	19.2(20)
F3	0.2680(23)	0.6285(9)	0.0263(13)	12.4(14)
F4	0.2832(24)	0.7966(12)	−0.0284(18)	18.1(20)
F5	0.1334(22)	0.7286(12)	0.0395(17)	15.5(17)
F6	0.4217(23)	0.6960(13)	−0.0516(14)	15.4(16)
P2	0.6984(10)	0.7900(5)	0.4896(6)	7.0(5)
F7	0.643(3)	0.7798(10)	0.5868(12)	13.4(15)
F8	0.752(3)	0.8018(12)	0.3930(12)	15.2(16)
F9	0.703(3)	0.8747(9)	0.5146(15)	14.8(16)
F10	0.6975(23)	0.7042(10)	0.4713(15)	13.5(15)
F11	0.8552(20)	0.7828(12)	0.5213(15)	14.3(16)
F12	0.5378(21)	0.7955(12)	0.4558(13)	13.4(14)

Table 3. Selected Bond Distances (Å) and Bond Angles (deg)

	Complex **7a**		
Fe−P	2.229(9)	FeA−PA	2.229(9)
Fe−C9	1.77(2)	FeA−C9A	1.80(2)
Fe−C10	1.67(3)	FeA−C10A	1.69(2)
C9−N	1.20(3)	C9A−NA	1.12(3)
N−C8	1.47(3)	NA−C8A	1.45(3)
C10−O10	1.16(3)	C10A−O10A	1.17(3)
C10−Fe−P	90(1)	C10A−FeA−PA	92.2(8)
C10−Fe−C9	96(1)	C10A−FeA−C9A	95(1)
C9−Fe−P	82.0(8)	C9A−FeA−PA	82.7(8)
Fe−C9−N	169(2)	FeA−C9A−NA	171(2)
C9−N−C8	141(2)	C9A−NA−C8A	142(2)
Fe−C10−O10	169(3)	FeA−C10A−O10A	177(2)
	Complex **18**		
Pd−Cl1	2.371(2)	Pd−N	2.067(5)
Pd−Cl2	2.277(2)	P2−N	1.575(6)
Pd−P1	2.203(2)		
Cl1−Pd−Cl2	91.17(8)	P1−Pd−N	83.5(2)
Cl2−Pd−P1	92.19(8)	P2−N−C8	119.4(4)
Cl2−Pd−N	175.1(2)	P2−N−Pd	125.6(3)
Cl1−Pd−P1	171.17(8)	C8−N−Pd	112.8(4)
Cl1−Pd−N	93.4(2)		

at ca. 2070 and 1955 cm^{-1} for the pentacarbonylmetal moiety. The ^{13}C NMR shifts of the isocyanide carbon appear at 162.5 ppm for **4**, 153.4 ppm for **5**, and 143.0 ppm for **6**, respectively. Both IR and NMR data indicate the existence of an isocyanide function. The formation of isocyanide complex is presumably proceeded by the nucleophilic attack of iminophosphorane at the carbonyl ligand followed by the elimination of triphenylphosphine oxide.[6] It appears that the carbonyl ligand of $M(CO)_6$ is more reactive toward nucleophilic attack by the iminophosphorane than that of $[M(CO)_5Br]^-$. Such a difference is believed due to the poorer M−C back-bonding of $M(CO)_6$ compared with that of $[M(CO)_5Br]^-$.

Reaction of phosphine−phosphinimine **1** with $CpFe(CO)_2I$ [Cp = η^5−C_5H_5] in toluene at 25 °C yielded a yellow precipitate {CpFe(CO)[CNCH$_2$CH$_2$CH$_2$PPh$_2$-*P*,*C*]}I (**7**) and triphenylphosphine oxide; the desired complex was purified by extraction of Ph_3P=O with toluene from the reaction mixture. Anionic metathesis of **7** with NH_4PF_6 gave {CpFe(CO)[CNCH$_2$CH$_2$CH$_2$-PPh$_2$-*P*,*C*]}PF_6 (**7a**) as a crystalline solid upon recrystallization. The phosphinimine function of **1** acts as a deoxygenating agent, which reacts with the carbonyl ligand to form an isocyanide moiety. In the infrared spectrum of **7**, the stretching wavenumbers corresponding to isocyanide (2089 cm^{-1}) and carbonyl (1998 cm^{-1}) were observed, clearly indicating the existence of both moieties around the metal center. An ORTEP plot of the cation of **7a** is illustrated in Figure 1. Atomic coordinates and selected bond distances and angles are listed in Tables 2 and 3, respectively. The iron atom displays a slightly distorted octahedral geometry with one face occupied by the cyclopentadienyl moiety. The Fe−C9 distance [1.77(2) Å] is smaller and the C9−N distance [1.20(3) Å] is larger than the average bond distance of Fe−C (1.84 Å) and C−N (1.17 Å) in complexes of Fe(*t*-BuNC)$_5$,[17] Fe(C$_6$H$_8$)(CO)$_2$(EtNC),[18] and Fe$_2$(EtNC)$_9$,[19] respectively. The angle C9−N−C8 [141-(2)°] is much deviated from 180°. All this information indicates that the nitrogen atom is no longer restrained in a linear environment, which implies that the reso-

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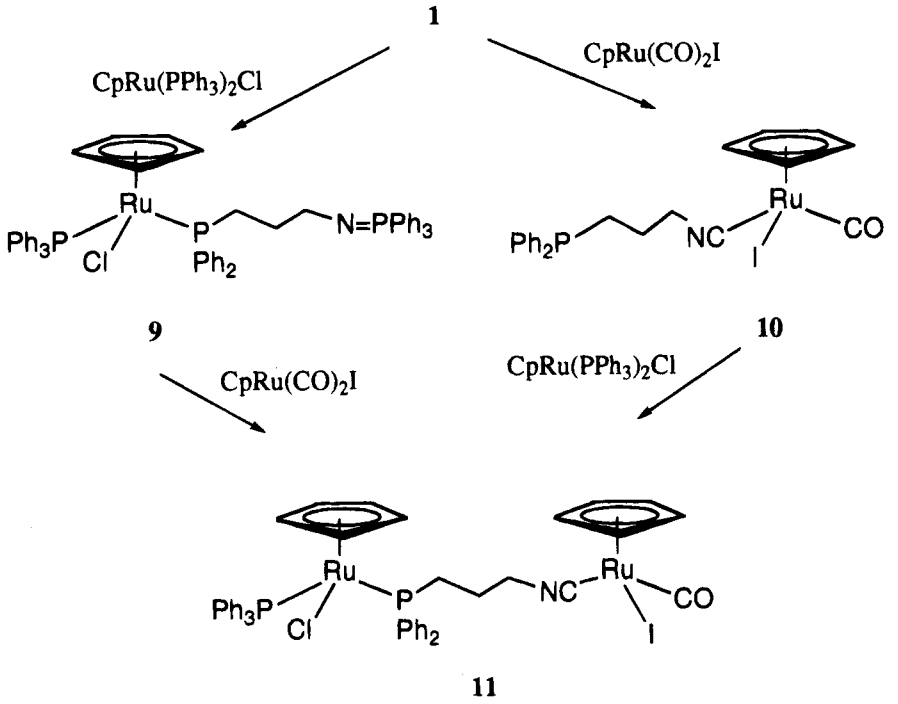
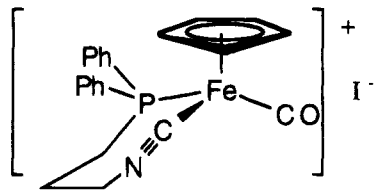
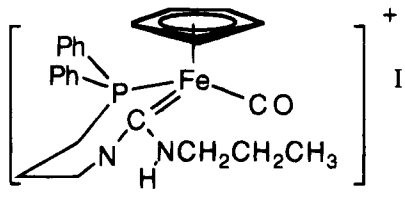
Scheme 2



nance form Fe=C=N− in the coordinated isocyanide group is much more important than Fe−C≡N−. This observation is also consistent with the smaller stretching wavenumber of isocyanide (2089 cm^{-1}) in **7** (Table 1) compared with $[CpFe(PPh_3)(CO)(CNCH_3)]BF_4$ (2194 cm^{-1}). Complex **7** readily reacted with propylamine to give carbene complex **8**. The structure of this carbene metal complex was determined by spectral and elemental analyses (Experimental Section).



7



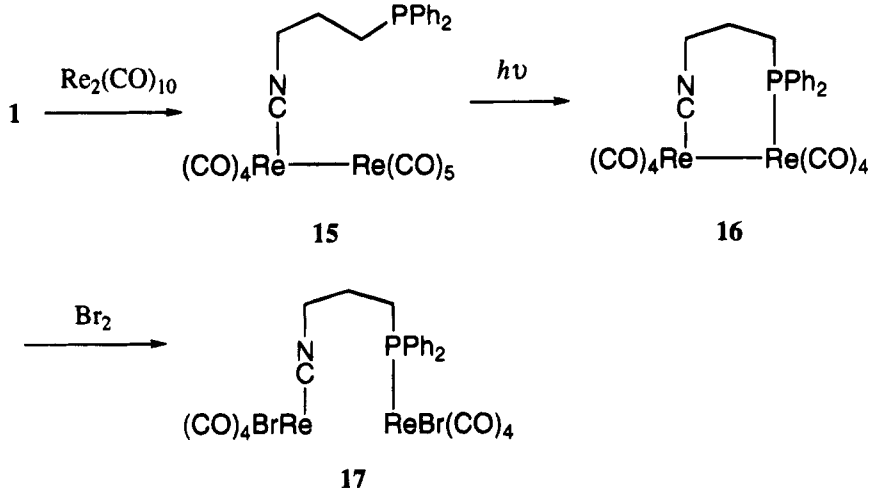
8

The chemistry of **1** toward ruthenium(II) complexes is summarized in Scheme 2. As expected, the ligand substitution reaction of $CpRu(PPh_3)_2Cl$ by the phosphino site of **1** took place immediately to yield the simple substituted complex **9**, but further substitution to form a σ-N and σ-P chelate complex did not occur, even under severe reaction conditions. Reaction of **1** with $CpRu(CO)_2I$ produced isocyanide complex **10** accompanied by formation of triphenylphosphine oxide. Unlike the iron complex, the diphenylalkylphosphine moiety in **10** remained as a free donor. Attempts to prepare a chelating mode of $CN(CH_2)_3PPh_2$ complex, like the iron analog, failed. Nevertheless, the uncoordinating donors in both **9** and **10** become an advantage in preparation of a binuclear species. Thus reaction of either complex **9** with $CpRu(CO)_2I$ or complex **10** with $CpRu(PPh_3)_2Cl$ yielded a bridging diruthenium complex **11**. As both ruthenium centers are chiral, the diastereomeric pair of complexes **11** were observed in ^{31}P NMR spectrum: one is 44.1 and 35.7 ppm; the other is 44.0 and 35.8 ppm. All these absorptions appear as doublets with phosphorus−phosphorus coupling constant 41 Hz. Attempts to separate these isomers by chromatography and recrystallization were unsuccessful.

The ruthenium complexes were characterized by spectral and elemental analyses. The ^{31}P NMR spectrum of complex **9** shows three sets of resonances: 44.1 (d, J = 41 Hz, PPh_3); 36.8 (d, J = 41 Hz, $-PPh_2$), and 13.0 (br, $-N{=}PPh_3$) ppm, in which the broad peak at 13.0 ppm corresponds to the free phosphinimine site. The naturally abundant ratio of ^{35}Cl and ^{37}Cl in the FAB mass spectrum of **9** indicates that the chloride is a coordinated ligand around the metal ion. The ^{31}P NMR spectrum of complex **10** shows only a signal due to a free diphenylalkylphosphine at δ −17.3 ppm, thus indicating that the phosphine moiety did not coordinate to the metal center and the phosphinimine function disappeared. Both infrared and ^{13}C NMR spectra of **10** show the presence of a coordinated isocyanide (2107 cm^{-1}) and a carbonyl ligand [IR 2107 cm^{-1} (NC) and 1973 cm^{-1} (CO); ^{13}C NMR δ 145.1 ppm (CN) and 199.5 ppm (CO)]. On this basis with elemental analysis the ruthenium complexes **10** and **11** were assigned as formulated.

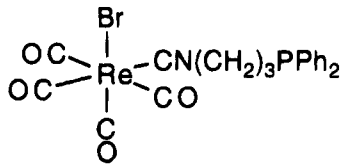
When $Re(CO)_5Br$ reacted with **1** under thermal conditions, deoxygenation at the carbonyl ligand occurred in dichloromethane solution to form an isocyanide complex **12**. The phosphine site of **1** in complex **12** remained a free donor, but it underwent further substitution with carbonyl ligands to give **13**. Treatment of **12** with **1** in a further equimolar quantity provided the diisocyanide

Scheme 3

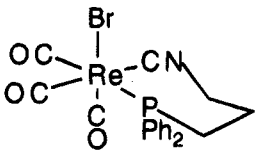


15 16 17

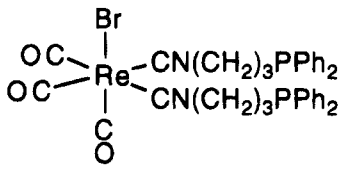
species **14** that has two free phosphine donors away from the metal center. The structures of **12**–**14** were confirmed by their spectral properties (see Experimental Section). The infrared stretching wavenumber of the isocyanide moiety (2138 cm^{-1}) in **13** is smaller than that of the other Re–CN species and the ^{13}C NMR shift of isocyanide carbon (δ 163 ppm) is also greater than those of related species (Table 1), similar to complex **7** due to ring strain.



12



13

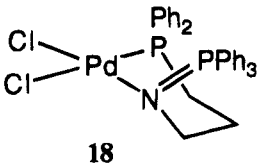


14

Reaction of phosphino–phosphinimine **1** with dirhenium decacarbonyl also yielded isocyanide complex **15** in which the phosphino site stays uncoordinated. On irradiation of **15** in chloroform with light, the phosphine exchanged a carbonyl ligand to form a bridging binuclear complex **16** (Scheme 3). Because of the ring strain of **16**, the properties of the coordinated isocyanide ligand in both infrared and ^{13}C NMR spectra show the same trend as in complexes **7** and **13**: a smaller wavenumber of the infrared stretching mode of CN– and a considerable downfield chemical shift of ^{13}C NMR of CN–. The lack of phosphorus–carbon coupling of the isocyanide carbon supports assignment of a structure in which $CN(CH_2)_3PPh_2$ binds in a bridging mode, not a chelating one. Upon treatment of **16** with bromine, the cleavage of the metal–metal bond of **16** occurred to yield $Br(CO)_4Re\{\mu_2\text{-}(CNCH_2CH_2CH_2PPh_2\text{-}C,P)\}Re(CO)_4Br$ (**17**). As the ring strain lessens, the spectral data for the coordinated isocyanide ligand of **17** exhibit the normal features; i.e. both the infrared absorption and ^{13}C NMR chemical shift of the isocyanide group are similar to those of non-chelate complexes (Table 1).

Addition of (cyclooctadiene)$PdCl_2$ to $Ph_3P{=}N(CH_2)_3PPh_2$ (**1**) in dichloromethane resulted in formation of palladium complex **18** as a yellow solid. This compound is stable, even in the presence of moisture. Complex **18** in chloroform-d_1 solution exhibited a pair of doublets in the ^{31}P NMR spectrum at 17.2 and 40.5 ppm with a coupling constant of 3.3 Hz, clearly indicating that both phosphinimine and phosphine are coordinated at the metal center. The formulation of **18** is further confirmed with X-ray structural analysis.

The results of an X-ray structural analysis of **18** are depicted in Figure 2 and in Tables 3 and 4. The coordination environment about the metal center in **18** is slightly distorted square-planar with the two chloride ligands situated in a *cis* fashion. All bond distances and bond angles in **18** are in the normal range. The Pd–Cl(1) bond [2.371(2) Å] is notably longer than Pd–Cl(2) [2.277(2) Å] which is an indication of the *trans* influence of phosphorus versus nitrogen donors. Attempts to prepare nickel and platinum analogs of **18** were unsuccessful.



18

Summary

We have demonstrated various reactions of the phosphinimine–phosphine $Ph_3P{=}N(CH_2)_3PPh_2$ (**1**) toward metal complexes. For coordination of phosphinimine, compound **1** acts as a σ-P donor (**I**), or in a σ-N and σ-P chelate fashion (**II**) (Chart 1). For deoxygenation of carbonyl, compound **1** becomes an isocyanide–phosphine ligand $CN(CH_2)_3PPh_2$, which acts as a σ-C donor (**III**), a σ-C and σ-P chelate (**IV**), a σ-C and σ-P bridging mode with a metal–metal bond (**V**), and a σ-C and σ-P bridging mode without a metal–metal bond (**VI**).

Experimental Section

General Information. Nuclear magnetic resonance spectra were recorded 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 instruments. The

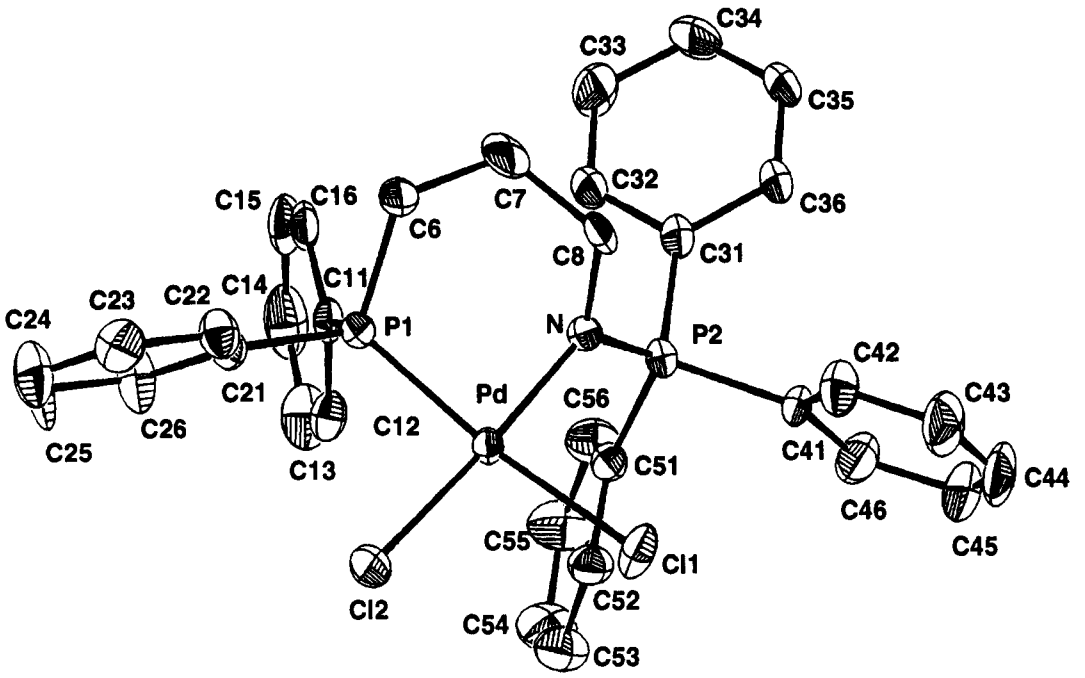


Figure 2. ORTEP diagram of palladium complex **18** showing 50% probability thermal ellipsoids.

Table 4. Atomic Coordinates and Thermal Parameters of 18

	x	*y*	*z*	B_{eq}, Å^2
Pd	0.40595(5)	0.76395(4)	0.05976(3)	2.54(3)
Cl1	0.22543(19)	0.70733(15)	−0.01970(10)	4.61(11)
Cl2	0.52498(20)	0.78297(15)	−0.02029(10)	4.66(11)
P1	0.55445(19)	0.83510(14)	0.13482(10)	2.83(10)
P2	0.26680(19)	0.65156(15)	0.16298(10)	2.98(10)
N	0.3129(5)	0.7467(4)	0.13834(24)	2.7(3)
C6	0.4730(7)	0.9220(5)	0.1750(4)	4.2(5)
C7	0.3599(8)	0.8910(6)	0.2035(5)	6.4(6)
C8	0.2576(7)	0.8336(5)	0.1581(4)	4.1(4)
C12	0.6423(6)	0.7590(5)	0.1982(3)	3.1(4)
C12	0.6773(7)	0.6732(5)	0.1780(4)	3.8(4)
C13	0.7457(8)	0.6116(6)	0.2223(4)	5.9(5)
C14	0.7754(8)	0.6339(7)	0.2878(4)	6.5(6)
C15	0.7430(7)	0.7182(6)	0.3104(4)	5.3(5)
C16	0.6774(6)	0.7817(6)	0.2640(4)	4.1(4)
C21	0.6784(7)	0.9023(5)	0.1059(4)	3.2(4)
C22	0.6451(7)	0.9803(5)	0.0694(4)	4.1(4)
C23	0.7382(8)	1.0339(6)	0.0477(4)	5.0(5)
C24	0.8623(8)	1.0063(6)	0.0621(5)	6.2(6)
C25	0.8989(8)	0.9304(7)	0.0984(5)	7.6(7)
C26	0.8097(7)	0.8747(6)	0.1205(5)	5.5(5)
C31	0.2620(7)	0.6629(5)	0.2483(4)	3.3(4)
C32	0.3749(7)	0.6830(6)	0.2937(4)	4.1(4)
C33	0.3779(8)	0.6959(6)	0.3611(4)	5.6(5)
C34	0.2595(8)	0.6904(6)	0.3828(4)	6.2(6)
C35	0.1490(7)	0.6709(6)	0.3386(4)	5.4(5)
C36	0.1471(7)	0.6569(6)	0.2726(4)	4.2(4)
C41	0.1064(7)	0.6102(5)	0.1214(4)	3.3(4)
C42	0.0163(7)	0.6708(6)	0.0862(4)	5.0(5)
C43	−0.1067(8)	0.6372(7)	0.0561(5)	6.6(6)
C44	−0.1337(8)	0.5477(7)	0.0619(5)	7.0(6)
C45	−0.0493(9)	0.4863(7)	0.0963(5)	7.1(6)
C46	0.0748(8)	0.5175(6)	0.1261(4)	5.1(5)
C51	0.3744(7)	0.5580(5)	0.1530(4)	3.1(4)
C52	0.3928(7)	0.5353(5)	0.0915(4)	3.9(4)
C53	0.4628(8)	0.4583(6)	0.0823(4)	5.3(5)
C54	0.5183(9)	0.4064(6)	0.1359(5)	6.2(5)
C55	0.5056(9)	0.4280(6)	0.1981(4)	6.2(6)
C56	0.4333(8)	0.5045(6)	0.2078(4)	4.9(5)

Table 5. Crystal Data for Complexes 7a and 18

	7a	18
formula	$C_{22}H_{21}F_6NOP_2Fe$	$C_{33}H_{31}Cl_2NP_2Pd$
fw	547.2	680.75
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
temp, K	298	298
a, Å	9.175(13)	10.460(3)
b, Å	17.514(9)	14.440(5)
c, Å	14.481(25)	20.558(8)
α, deg	90.51(8)	
β, deg	92.28(12)	101.99(3)
γ, deg	90.61(8)	
V, Å^3	2325(5)	3038(2)
2θ range, deg	18.68−26.30	19.28−24.84
F(000)	1112	1384
Z	4	4
D_{calcd}, g cm^{-3}	1.563	1.489
μ, cm^{-1}	8.440	9.757
scan width	ω−2θ	ω−2θ
radiation	Mo Kα	Mo Kα
cryst dimens, mm	0.20 × 0.30 × 0.35	0.30 × 0.30 × 0.35
scan width	2(1.00 + 0.35 tan θ)	2(0.90 + 0.35 tan θ)
transm range	0.551, 1.00	0.913, 1.00
$2\theta_{max}$, deg	45.0	45.0
no. of unique reflns	6055	3962
no. of reflns obsd[a]	1868	2821
computation	NRCSDP-VAX	NRCSDP-VAX
soln method	heavy atom	heavy atom
no. of params	475	352
R	0.089	0.044
R_w	0.084	0.033
S	2.67	2.51

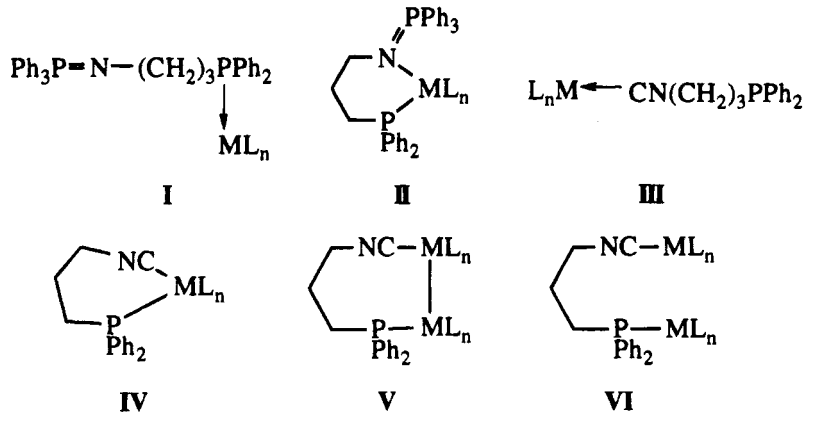
[a] $I > 2\sigma(I)$. [b] $R = \Sigma|F_o - F_c|/\Sigma(F_o)$; $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2}$; $S = [\Sigma w(F_o - F_c)^2/(\text{no. of reflns} - \text{no. of params})$.

photochemical apparatus was a 450 W Conrad-Hanovia medium-pressure mercury lamp (Ace Glass).

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 and toluene were 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.

***N*-(3-(Diphenylphosphino)propyl)triphenylphosphinimine, 1.** To a benzene solution of 3-azidopropyl chloride (4.74 g, 39.6 mmol) was added a benzene solution of triphenylphosphine (10.4 g, 39.6 mmol). The resulting solution was stirred for 8 h, and the solvent was removed under reduced pressure. A white solid of (3-chloropropyl)tri-

Chart 1



phenylphosphinimine (15.14 g, 100%) was obtained, which was characterized by spectral methods: ^{1}H NMR δ 7.70–7.25 (m, 15 H, Ar *H*), 3.67 (t, J = 6.6 Hz, 2 H, $-CH_2Cl$), 3.20 (dt, J = 16, 6.4 Hz, 2 H, $-CH_2NP-$), 1.95 (dtt, J = 1.2, 6.4, 6.4 Hz, 2 H, $-CH_2-$); ^{13}C NMR δ (aliphatic carbon) 43.6 ($-CCl$), 42.1 (d, J_{P-C} = 4.4 Hz, $-CN{=}P$), 37.8 (d, J_{P-C} = 18.7 Hz, $-CH_2-$); ^{31}P NMR δ 12.4.

A solution of diphenylphosphide anion was prepared by the addition of a 1.6 M hexane solution of *n*-butyllithium (25 mL, 40 mmol) to a THF solution (100) mL) of diphenylphosphine (7.4 g, 39.7 mmol). This anion solution was then added to a solution of (3-chloropropyl)triphenylphosphinimine (15.4 g) in THF (100 mL) with stirring. The resulting mixture was kept stirred for 4 h, and solvents were removed under reduced pressure. The residue was dissolved in benzene and filtered. The filtrate was concentrated and recrystallized from acetonitrile to give the desired compound **1** as a white solid (13.2 g, 66%), which is quite sensitive to moisture: mp 120–122 °C; ^{1}H NMR (C_6D_6) δ 7.80–7.50 (m, 12 H, Ar *H*), 7.15–6.95 (m, 13 H, Ar *H*), 3.50 (dt, J = 16, 6.4 Hz, 2 H, $-CH_2N$), 2.41 (m, 2 H, $-CH_2P-$), 2.08 (m, 2 H, $-CH_2-$); ^{13}C NMR δ (aliphatic carbon) 46.8 (dd, J = 14.4, 4.6 Hz, $-CNP-$), 32.7 (dd, J = 20.9, 14.8 Hz, $-CPPh_2$), 26.4 (d, J = 11.5 Hz, $-CH_2-$); ^{31}P NMR (C_6D_6) δ 4.3, −16.0; ^{31}P NMR ($CDCl_3$) δ 12.1 (br), −15.0. HRMS Calcd for $C_{33}H_{31}NP_2$: m/z 503.1932. Found: m/z = 503.1933. Anal. Calcd for $C_{33}H_{31}NP_2$: C, 78.71; H, 6.21; N, 2.78. Found: C, 78.52; H, 6.26; N, 2.75.

{$Ph_2P(CH_2)_3NPPh_3$-*P,N*}$Mo(CO)_4$ (2). A mixture of **1** (201 mg, 0.40 mmol) and $Et_4N[Mo(CO)_5Br]$ (175 mg, 0.38 mmol) in THF (10 mL) was heated to reflux for 8 h. The reaction mixture was filtered, and the filtrate was concentrated to give the desired complex **2** as a yellow solid (175 mg, 66%): mp 125–138 °C dec; IR (THF) ν_{CO} 2004, 1891, 1875, 1843 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.71–7.20 (m, 25 H, Ar *H*), 3.47 (dm, J_{P-H} = 20.7 Hz, 2 H, $-CH_2NP-$), 2.62 (m, 2 H, $-CH_2P-$), 1.64 (m, 2 H, $-CH_2-$); ^{13}C NMR δ (aliphatic) 54.8 (d, J = 5.1 Hz, $-CH_2-NP-$), 29.3 (d, J = 15.1 Hz, $-CPPh_2$), 28.0 (d, J = 8.6 Hz, $-CH_2-$); ^{31}P NMR δ 39.4 (d, J = 14 Hz), 16.3 (d, J = 14 Hz). Anal. Calcd for $C_{37}H_{31}NO_4P_2Mo$: C, 62.46; H, 4.39; N, 1.97. Found: C, 62.00; H, 4.80; N, 1.86.

{$Ph_2P(CH_2)_3NPPh_3$-*P,N*}$W(CO)_4$ (3). The preparation of **3** was similar to the procedure described for **2**. Complex **3** is a yellow solid: mp 179–186 °C dec; IR (THF) ν_{CO} 1998, 1881, 1863, 1838 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.22–7.40 (m, 25 H, Ar *H*), 3.67 (dm, J_{P-H} = 19.5 Hz, 2 H, $-CH_2NP-$), 2.77 (m, 2 H, $-CH_2P-$), 1.67 (m, 2H, $-CH_2-$); ^{13}C NMR δ (aliphatic) 56.1 (d, J = 5.7 Hz, $-CNP-$), 29.4 (d, J = 18.5 Hz, $-CPPh_2$), 27.8 (d, J = 8.3 Hz, $-CH_2-$); ^{31}P NMR δ 37.9 (d, J = 18 Hz), 2.67 (dt, J_{P-P} = 18 Hz, J_{P-W} = 224 Hz). Anal. Calcd for $C_{37}H_{31}NO_4P_2W$: C, 55.59; H, 3.91; N, 1.75. Found: C, 55.20; H, 3.90; N, 2.10.

General Procedure for Preparation of $M(CO)_5(CNCH_2CH_2CH_2PPh_2$-*C*) [M = Cr, Mo, W]. A mixture of $M(CO)_6$ and **1** in equimolar quantity in THF was stirred at 25 °C for 40 h. The reaction mixture was concentrated, and the residue was chromatographed on silica gel with elution of dichloromethane. A yellow band was collected and concentrated to give the desired product.

{$Ph_2P(CH_2)_3NC$-*C*}$Cr(CO)_5$ (4). A yellow liquid (46% yield): IR (CH_2Cl_2) ν_{CN} 2173 cm^{-1}, ν_{CO} 2066, 1955 cm^{-1}; ^{1}H NMR δ 7.47–7.32 (m, 10 H, Ar *H*), 3.65 (t, J = 6.4 Hz, 2 H, $-NCH_2$), 2.18 (m, 2 H, $-CH_2P-$), 1.85 (m, 2 H, $-CH_2-$); ^{13}C NMR δ 216.9, 214.9, 162.5 (*C*N−), 137.5 (d, J = 11 Hz), 132.6 (d, J = 19 Hz), 129.0, 128.7 (d, J = 5.8 Hz), 45.3 (d, J = 14.3 Hz), 26.1 (d, J = 19.3 Hz, $-CH_2P-$), 25.0 (d, J = 12.7 Hz, $-CH_2-$); ^{31}P NMR δ −17.66. Anal. Calcd for $C_{21}H_{16}NO_5PCr$: C, 56.64; H, 3.62; N, 3.15. Found: C, 56.60; H, 3.10; N, 2.94.

{$Ph_2P(CH_2)_3NC$-*C*}$Mo(CO)_5$ (5). A yellow liquid (50%): IR (CH_2Cl_2) ν_{CN} 2173 cm^{-1}, ν_{CO} 2071, 1952 cm^{-1}; ^{1}H NMR δ 7.51–7.33 (m, 10 H, Ar *H*), 3.67 (t, J = 6.5 Hz, 2 H, $-NCH_2-$), 2.21 (m, 2 H, $-CH_2PPh_2$), 1.89 (m, 2 H, $-CH_2-$); ^{13}C NMR δ 206.7, 203.8, 153.4 (*C*N−), 137.4 (d, J = 12.5 Hz), 132.5 (d, J = 19 Hz), 129.0, 128.6 (d, J = 6.8 Hz), 44.8 (d, J = 14.3 Hz), 25.9 (d, J = 18.2 Hz), 24.9 (d, J = 13.7 Hz); ^{31}P NMR δ −17.71. Anal. Calcd for $C_{21}H_{16}NO_5PMo$: C, 51.55; H, 3.30; N, 2.80. Found: C, 51.52; H, 3.40; N, 2.83.

{$Ph_2P(CH_2)_3NC$-*C*}$W(CO)_5$ (6). A yellow liquid (67%): IR (CH_2Cl_2) ν_{CN} 2175 cm^{-1}, ν_{CO} 2068, 1956 cm^{-1}; ^{1}H NMR δ 7.47–7.32 (m, 10 H, Ar *H*), 3.72 (t, J = 6.5 Hz, 2 H, $-NCH_2$), 2.19 (m, 2 H, $-CH_2P-$), 1.89 (m, 2 H, $-CH_2-$); ^{13}C NMR δ 196.1, 194.3, 143.0, 137.4 (d, J = 12.3 Hz), 132.6 (d, J = 18.2 Hz), 129.0, 128.7 (d, J = 6.9 Hz), 45.0 (d, J = 14.2 Hz), 26.10 (d, J = 18.3 Hz), 25.0 (d, J = 12.9 Hz); ^{31}P NMR δ −17.75. Anal. Calcd for $C_{21}H_{16}NO_5PW$: C, 43.70; H, 2.79; N, 2.43. Found: C, 43.77; H, 2.76; N, 2.44.

[{$Ph_2P(CH_2)_3NC$-*P,C*}Fe(CO)] (7). A solution of $CpFe(CO)_2I$ (75.9 mg, 0.25 mmol) and **1** (126 mg, 0.25 mmol) in toluene (20 mL) was stirred at room temperature for 4 h. A yellow precipitate formed during the reaction was collected by filtration. The yellow solid was washed with toluene and hexane to give the pure complex **7** (110 mg, 83%): mp 165–169 °C dec; IR ($CHCl_3$) 2089 (ν_{CN}), 1998 cm^{-1} (ν_{CO}); ^{1}H NMR ($CDCl_3$) δ 7.64–7.13 (m, 10 H), 4.97 (s, 5 H), 4.57–4.48 (m, 1 H), 3.67–3.56 (m, 1 H), 3.50–3.42 (m, 1 H), 2.74–2.62 (m, 1 H), 2.30–2.20 (m, 1 H), 2.20–2.05 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 213.0 (d, J = 22.3 Hz, $-CO$), 183.7 (d, J = 35.1 Hz, $-NC$), 133.9, 128.1 (m), 48.9, 32.0 (d, J = 31 Hz), 28.8 (d, J = 4.8 Hz); ^{31}P NMR ($CDCl_3$) δ 54.0; FAB m/z = 402. Anal. Calcd for $C_{22}H_{21}INPOFe$: C, 49.94; H, 4.00; N, 2.65. Found: C, 49.59; H, 4.05; N, 2.53.

[{$Ph_2P(CH_2)_3NC$-*P,C*}Fe(CO)]PF_6 (7a). A solution of **7** and excess NH_4PF_6 in acetone was stirred for 4 h. The reaction mixture was filtered and concentrated, and the residue was recrystallized from a mixed solvent (hexane/CH_2Cl_2) to give **7a** as a yellow solid quantitatively: mp 175–180 °C dec; IR (KBr) 2098 (ν_{CN}), 2011 cm^{-1} (ν_{CO}); ^{1}H NMR ($CDCl_3$) δ 7.64–7.13 (m, 10 H, Ar *H*), 4.87 (s, 5 H, Cp *H*), 4.03 (m, 1 H), 3.50

(m, 1 H), 2.96 (m, 1 H), 2.60 (m, 1 H), 2.20 (m, 1 H), 2.00 (m, 1 H); ^{31}P NMR ($CDCl_3$) δ 54.0, −143.6 (PF_6).

[{$Ph_2P(CH_2)_3NH(n$-PrNH)C=}Fe(CO)]I (8). A mixture of *n*-propylamine (5 mL) and **7** (450 mg, 0.166 mmol) in dichloromethane (20 mL) was stirred at 25 °C for 1 h. On removal of the solvent, the residue was crystallized from chloroform and pentane to give **8** as a yellow crystalline solid (435 mg, 87%): mp 185−190 °C dec; IR (CH_2Cl_2) ν(CO) 1949 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.31 (br, 1 H), 7.49−7.12 (m, 10 H), 6.40 (br, 1 H), 4.53 (s, 5 H), 4.35 (m, 1 H), 3.60 (m, 2 H), 3.50 (m, 1 H), 2.79 (m, 2 H), 2.17 (m, 1 H), 2.11 (m, 2 H), 1.30 (m, 1 H), 1.11 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 218.6 (d, J = 31.8 Hz), 209.8 (d, J = 25.6 Hz), 139.2 (d, J = 48.3 Hz), 132.9 (d, J = 47 Hz), 132.8 (d, J = 9.4 Hz), 131.02 (d, J = 1.9 Hz), 130.2 (d, J = 1.7 Hz), 130.0 (d, J = 8.6 Hz), 129.0 (d, J = 9.5 Hz), 128.6 (d, J = 9.8 Hz), 84.7, 48.2, 45.5, 35.5 (d, J = 22 Hz), 24.8, 21.9, 11.6; ^{31}P NMR ($CDCl_3$) δ 56.5. Anal. Calcd for $C_{25}H_{30}IN_2POFe$: C, 51.05; H, 5.14; N, 4.76. Found: C, 52.12; H, 5.07; N, 4.84.

[CpRu{$Ph_2P(CH_2)_3NPPh_3$-*P*}(PPh_3)Cl] (9). A mixture of $CpRu(PPh_3)_2Cl$ (634 mg, 0.873 mmol) and **1** (440 mg, 0.873 mmol) in benzene (40 mL) was heated to reflux for 4 h. The benzene solvent was replaced by ether, and a yellow precipitate was formed and collected. The precipitate was subsequently washed with ether (20 mL × 2) to give complex **5** as a yellow solid (570 mg, 68%): mp 122−125 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.80−6.95 (m, 40 H), 4.03 (s, 5 H), 2.61 (dt, J = 20, 7.8 Hz, 2 H), 2.21−2.11 (m, 1 H), 1.38−1.20 (m, 1 H), 0.80−0.60 (m, 2 H); ^{13}C NMR δ (aliphatic) 80.5, 43.0 (d, J = 11.6 Hz), 28.4 (d, J = 8.9 Hz), 18.9 (dd, J = 38.7, 20 Hz); ^{31}P NMR δ 44.1 (d, J = 41.4 Hz), 36.8 (d, J = 41.4 Hz), 13.0 (br); FAB (m + 1)/z = 968. Anal. Calcd for $C_{56}H_{51}NP_3RuCl$: C, 69.52; H, 5.31; N, 1.45. Found: C, 69.31; H, 5.24; N, 1.57.

[CpRu{$Ph_2P(CH_2)$NC-*C*}(CO)I] (10). To a solution of $CpRu(CO)_2I$ (200 mg, 0.57 mmol) in dichloromethane was added compound **1** (302 mg, 0.60 mmol); the resulting mixture was stirred at room temperature for 10 h. Removal of solvent yielded a liquid residue, which was chromatographed on alumina (10 g) with elution with dichloromethane. A red band eluate was collected and concentrated to give the complex **6** as a red liquid (272 mg, 83%): IR (CH_2Cl_2) ν(−NC) 2170, ν(−CO) 1973 cm^{-1}; ^{1}H NMR δ 7.46−7.24 (m, 10 H), 5.14 (s, 5 H), 3.82 (t, J = 6.4 Hz, 2 H), 2.25−2.19 (m, 2 H), 1.92−1.79 (m, 2 H); ^{13}C NMR δ 199.5 (−*C*O), 145.1 (*C*N−), 137.5−128.6 (Ar *C*), 84.4 (Cp−), 45.7 (d, J = 14.5 Hz), 26.3 (d, J = 18.1 Hz), 24.8 (d, J = 11.9 Hz); ^{31}P NMR δ −17.3. Anal. Calcd for $C_{22}H_{21}INOPRu$: C, 46.01; H, 3.69; N, 2.44. Found: C, 45.78; H, 3.69; N, 2.46.

[Cp(PPh_3)ClRu{μ-$Ph_2P(CH_2)_3$NC-*P,C*}RuCp(CO)I] (11). Method 1. A mixture of **9** (140 mg, 0.144 mmol) and $CpRu(CO)_2I$ (50.4 mg, 0.144 mmol) in toluene (10 mL) was stirred at room temperature for 10 h. Concentration of the reaction mixture gave the crude product as a red solid, which was purified by chromatography on alumina with elution of dichloromethane. Recrystallization from $CHCl_3$/pentane at −20 °C provided the desired complex **11** as an orange crystalline solid (107 mg, 72%).

Method 2. A benzene solution of **10** (60 mg, 0.104 mmol) and $CpRu(PPh_3)_2Cl$ (75.8 mg, 0.104 mmol) was heated to reflux for 4 h. Replacement of benzene with ether solvent yielded a red precipitate solid, which was washed with ether (20 mL, ×2) to provide pure **11** as an orange-red solid (63 mg, 58%).

Both methods provided formation of diastereomeric pairs of **11**, which could not be separated at present. IR (CH_2Cl_2): ν(−NC) 2170, ν(−CO) 1970 cm^{-1}. ^{1}H NMR: δ 7.90−7.88 (m, 2 H), 7.50−7.04 (m, 23 H), 5.14 (s, 5 H), 4.13 (s, 5 H), 3.31−3.13 (m, 2 H), 2.31−2.22 (m, 1 H), 1.29−1.21 (m, 1 H), 1.10−1.00 (m, 1 H), 0.88−0.74 (m, 1 H). ^{31}P NMR: δ 44.12 (d, J = 41.4 Hz), 35.74 (d, J = 41.4 Hz) as one pair of diastereomers; δ 44.05 (d, J = 41.4 Hz), 35.78 (d, J = 41.4 Hz). Anal. Calcd for $C_{45}H_{41}ClINOP_2Ru_2$·0.5$CHCl_3$: C, 49.77; H, 3.81; N, 1.24. Found: C, 49.28; H, 3.74; N, 1.24.

$Br(CO)_4Re(CNCH_2CH_2PPh_2$-*C*) (12). A mixture of $Re(CO)_5Br$ (73 mg, 0.18 mmol) and **1** (90.5 mg, 0.18 mmol) in CH_2Cl_2 (10 mL) was heated to reflux for 2 h. Ather removal of solvent, the residue was chromatographed on silica gel with dichloromethane as the eluent. The eluate was collected and concentrated to give the desired complex **12** as a colorless liquid (75 mg, 66%): IR (CH_2Cl_2) ν_{CN} 2222 cm^{-1}, ν_{CO} 2112, 2020, 1958 cm^{-1}; ^{1}H NMR δ 7.47−7.30 (m, 10 H, Ar *H*), 3.87 (t, J = 6.5 Hz, 2 H, −NCH_2−), 2.22 (m, 2 H, −PCH_2−), 1.93 (m, 2 H, −CH_2−); ^{13}C NMR δ 182.3, 181.1, 180.1 (−*C*O), 137.2 (d, J = 11.2 Hz), 132.6 (d, J = 19.2 Hz), 129.0, 128.6 (d, J = 6.8 Hz) (Ar *C*), 129.2 (−*C*N), 45.4 (d, J = 15.1 Hz, −NCH_2−), 25.6 (d, J = 18.7 Hz, −PCH_2−), 24.7 (d, J = 13.2, −CH_2−); ^{31}P NMR δ −17.83. Anal. Calcd for $C_{20}H_{16}BrNPO_4Re$: C, 38.04; H, 2.22; N, 2.55. Found: C, 37.95; H, 2.31; N, 2.52.

$Br(CO)_3Re(CNCH_2CH_2CH_2PPh_2$-*P,C*) (13). A solution of **12** (50 mg, 0.08 mmol) in benzene (10 mL) was heated to reflux for 4 h. The reaction mixture was chromatographed on silica gel (5 g) with elution with CH_2Cl_2. The eluate was collected and concentrated to give **13** as a clear colorless liquid (35 mg, 73%): IR ν_{CN} 2137 cm^{-1}, ν_{CO} 2039, 1975, 1917 cm^{-1}; ^{1}H NMR δ 7.68−7.36 (m, 10 H), 4.00 (m, 1 H), 3.44 (m, 2 H), 2.76 (m, 1 H), 2.07 (m, 2 H); ^{13}C NMR δ 190.2 (d, J = 8.9 Hz), 187.83 (d, J = 58.5 Hz), 187.78 (d, J = 6.2 Hz) (−CO), 163.0 (d, J = 6.8 Hz, −*C*N), 134.3−128.0 (Ar *C*), 47.2, 28.7 (d, J = 2.7 Hz), 27.7 (d, J = 28 Hz); ^{31}P NMR δ −4.33. Anal. Calcd for $C_{19}H_{16}NPO_3ReBr$: C, 37.82; H, 2.67; N, 2.32. Found: C, 37.57; H, 2.73; N, 2.30.

$(CO)_3BrRe(CNCH_2CH_2CH_2PPh_2$-*C*)$_2$ (14). A mixture of **1** (920 mg, 1.827 mmol) and $BrRe(CO)_5$ (370 mg, 0.911 mmol) in benzene (40 mL) was stirred at 25 °C for 10 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 **14** as a colorless liquid (565 mg 73%): IR ($CHCl_3$) 2219 (ν_{CN}), 2041, 1981, 1926 cm^{-1} (ν_{CO}): ^{1}H NMR δ 7.47−7.31 (m, 20 H, Ar *H*), 3.68 (t, J = 6.4 Hz, 4 H, CNCH_2−), 2.17 (m, 4 H, −C$H_2$$PPh_2$), 1.83 (m, 4 H, −C$H_2$−); ^{13}C NMR δ 186.1, 183.8, 137.1 (d, J = 8.6 Hz), 137.0 (d, J = 8.9 Hz), 134.3 (−*C*N), 132.4 (d, J = 6.8 Hz), 132.2 (d, J = 6.6 Hz), 128.7, 128.6, 128.3 (d, J = 6.6 Hz), 44.6 (d, J = 14.5 Hz), 25.3 (d, J = 18.5 Hz), 24.2 (d, J = 13.1 Hz); ^{31}P NMR δ −17.80; FABMS (m + 1)/z = 857.0. Anal. Calcd for $C_{35}H_{32}N_2P_2O_3ReBr$: C, 49.07; H, 3.76; N, 3.27. Found: C, 49.01; H, 3.80; N, 3.26.

$(CO)_9Re_2(CNCH_2CH_2CH_2PPh_2$-*C*) (15). A solution of **1** (42 mg, 0.083 mmol) and $Re_2(CO)_{10}$ (54 mg, 0.083 mmol) in toluene (10 mL) was stirred at 25 °C for 10 h. The reaction mixture was chromatographed on silica gel with dichloromethane as the eluent. Upon concentration of the eluate, the desired product was obtained as a colorless liquid (67 mg, 92%): IR 2187 (ν_{CN}), 2099, 2074, 2046, 2008, 1994, 1968, 1942 cm^{-1} (ν_{CO}); ^{1}H NMR δ 7.50−7.33 (m, 10 H), 3.85 (t, J = 6.7 Hz, 2 H), 2.12 (m, 2 H), 1.85 (m, 2 H); ^{13}C NMR δ 194.6, 192.0, 184.6 (−CO), 134.5 (−*C*N), 137.3 (d, J = 12 Hz), 132.6 (d, J = 19.3 Hz), 129.0 128.7 (d, J = 7.6 Hz) (Ar *C*), 45.6 (d, J = 14.4 Hz), 25.8 (d, J = 19.5 Hz), 25.0 (d, J = 13.9 Hz); ^{31}P NMR δ −17.5. Anal. Calcd for $C_{25}H_{16}NO_9Re_2$: C, 34.21; H, 1.84; N, 1.60. Found: C, 34.32; H, 1.80; N, 1.59.

$(CO)_4Re${μ_2-$CNCH_2CH_2CH_2PPH_2$-*P,C*}$Re(CO)_4$ (16). A solution of **15** (640 mg, 0.729 mmol) in chloform was irradiated with light for 2 h. After concentration, the residue was chromatographed on silica gel with dichloromethane as eluent. The eluate was concentrated to give the desired product **16** as a white solid (450 mg, 73%): mp 165−185 °C dec; IR (KBr) ν 2156 (−CN), 2081, 2062, 2034, 1973, 1958 cm^{-1} (−CO); ^{1}H NMR δ 7.64−7.47 (m, 10 H), 3.86 (t, J = 6 Hz, 2 H), 2.92 (m, 2 H), 1.83 (m, 2 H); ^{13}C NMR δ 185.4 (d, J = 9 Hz), 183.5, 183.3 (d, J = 7 Hz), 182.8, 182.1, 180.6, 178.9 (*C*N−), 132.3, 132.2 (d, J = 10.5 Hz), 131.5 (d, J = 2 Hz), 129.4 (d, J = 9.7 Hz), 45.2 (d, J = 17 Hz), 23.5, 22.9 (d, J = 30 Hz); ^{31}P NMR δ −0.3. Anal. Calcd for $C_{24}H_{16}NO_8Re_2$: C, 35.21; H, 1.97; N, 1.71. Found: C, 34.93; H, 2.05; N, 1.69.

$Br(CO)_4Re\{\mu_2$-$CNCH_2CH_2CH_2PPh_2$-*P,C*$\}Re(CO)_4Br$ (17). Bromine (31 mg, 0.194 mmol) was added to a solution of **16** (140 mg, 0.166 mmol) in dichloromethane (100 mL) at room temperature. After stirring for 3 h, the reaction mixture was concentrated and the residue was chromatographed on silica gel with ethyl acetate and hexane (1/4) as the eluent. The eluate was collected and concentrated to give **17** as a clear, colorless liquid (125 mg, 75%): IR (CH_2Cl_2) 2221 cm^{-1} (−CN), 2110, 2021, 1954 cm^{-1} (−CO); ^1H NMR δ 7.62−7.47 (m, 10 H), 3.88 (t, J = 6 Hz, 2 H), 3.02 (m, 2 H), 1.80 (m, 2 H); ^{13}C NMR δ 184.2 (d, J = 9.2 Hz), 182.5 (d, J = 6.6 Hz), 182.3, 181.7, 181.0, 179.9, 132.0 (d, J = 10.6 Hz), 131.4, 131.3, 130.7, 129.1 (d, J = 9.8 Hz), 44.8 (d, J = 17 Hz), 24.1 (d, J = 31.3 Hz), 23.2; ^{31}P NMR δ −5.12. Anal. Calcd for $C_{24}H_{16}Br_2NO_8Re_2$: C, 29.46; H, 1.65; N, 1.43. Found: C, 29.31; H, 1.75; N, 1.42.

$Cl_2Pd(Ph_2PCH_2CH_2CH_2NPPh_3$-*P,N*) (18). A mixture of **1** (106 mg, 0.21 mmol) and $Pd(COD)Cl_2$ (60 mg, 0.21 mmol) in dichloromethane (15 mL) was stirred at 25 °C for 8 h. On removal of solvents, the residue was dissolved in chloroform and pentane and the desired complex **18** crystallized as a yellow-orange solid (136 mg, 95%): mp 154−158 °C dec; ^1H NMR δ 7.67−7.33 (m, 25 H), 3.21 (m, 2 H), 2.05 (m, 2 H), 1.86 (m, 2 H); ^{13}C NMR δ (aliphatic) 45.5 (d, J = 2.9 Hz), 25.3 (d, J = 9.5 Hz), 22.5 (d, J = 33.5 Hz); ^{31}P NMR δ 40.5 (d, J = 3.3 Hz), 17.2 (d, J = 3.3 Hz). Anal. Calcd for $C_{33}H_{31}Cl_2NP_2Pd$: C, 58.21; H, 4.59; N, 2.06. Found: C, 58.19; H, 4.84; N, 1.81.

X-ray Crystallography. Single crystals suitable for X-ray analysis of complexes **7a** and **18** were obtained in each case by slow evaporation of a chloroform/pentane solution under air. Cell parameters were determined on a CAD-4 diffractometer at 298 K by a least-squares treatment. Atomic scattering factors were taken from ref 24. The NRCC SDP VAX program was used for calculation.[25] Crystal data of these complexes are summarized in Table 5, and their non-hydrogen atomic coordinates are listed in Tables 2 and 4, respectively.

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Supplementary Material Available: Anisotropic thermal parameters and complete bond distances and bond angles for **7a** and **18** (7 pages). Ordering information is given on any current masthead page.

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