end-on coordination is more favorable than the side-on one. Hereafter, the former coordination will be discussed by comparing the theoretical consideration with experimental data.

Comparison with Experimental Results

As a result of the present considerations, it is found that both the σ donation and the π back-donation contribute to the formation of the M–N bond, and the former is more important than the latter. Furthermore, the weakening of the N–N bond due to the formation of the dinitrogen complex is found to be ascribable to the π back-donation. Therefore, it is considered that the observed ν_{NN} values are primarily related not to the strength of the M–N bond but to the magnitude of the π back-donation.

The magnitude of the π back-donation is clearly related to the energy levels of the d orbitals of the central metal atom. Since these values are, in general, parallel to the transition series 3d < 4d < 5d, the N–N frequencies, which may be expected by the strength of the π back-donation, are parallel to the transition series.[23] Experimental results reported so far are summarized in Table IV, in which complexes are coordinated with the same ligands but are changed by the central atoms of the same group of the different transition series. In the $M(NH_3)_5(N_2)^{2+}$-type complexes[21] (M = Ru, Os), the ν_{NN}'s decrease in the order Ru (4d) > Os (5d), and other pairs of the dinitrogen complexes indicate the same trend, being consistent with the present prediction. Moreover, the Os(III) complex is a weaker electron donor than the Os(II) complex. The former has a strong N–N bond in comparison with the latter. The same result is seen in the Re complexes.

While the N–N bond strength has the parallel relationship with the transition series, the M–N bond strength is not so simple, because this is affected by the contribution from the π back-donation as well as the σ donation even though the bond itself is formed mainly by the σ donation. For example, the M–N bond in $Os(NH_3)_5(N_2)^{2+}$ is stronger than that in the Ru analogue.[24] It may be attributed to the larger π back-donation of the Os complex. On the other hand, a complex, $Fe(Et_2PC_2H_4PEt_2)_2H(N_2)$, has been synthesized, but the Ru and Os analogues have not been done yet.[2] It is considered that there is not σ donation enough to form the stable Os or Ru complex, probably because of the higher energy levels of the unoccupied d_{z^2} or sp orbitals of metals owing to the electron transfer from $Et_2PC_2H_4PEt_2$ ligands.

Concluding Remarks

In the present work, the dinitrogen complexes of transition metals are investigated in terms of the MO calculations and the mode of orbital interactions. The calculated results, in the light of experimental data reported so far, suggest the following.

(1) Both the σ donation and the π back-donation are related to the formation of the metal–nitrogen bond in dinitrogen complexes. The former interaction is more important to it than the latter one. The π back-donation contributes to the weakening of the N–N bond.

(2) The N–N bond of the side-on complex is appreciably weakened because of the electron donation from the bonding π orbital and σ orbital of the N_2 ligand to the unoccupied MO's of the metal. Moreover, there is the electron acceptance from the occupied MO's of the latter to the antibonding π^* of the former. Therefore, the end-on coordination is considered to be more advantageous than the side-on one. The weak N–N bond in the side-on complex indicates that the N_2 ligand in this type complex is fairly activated. It may be suggested that the reduction of the coordinated nitrogen molecule proceeds through this activated form.[25]

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Registry No. 1, 19504-40-6; **2**, 73466-70-3; **3**, 73466-71-4; N_2, 7727-37-9.

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[23] The first transition series is that of metals which have 3d valence orbitals. The second and third ones are those of metals with 4d and 5d valence orbitals, respectively.

[24] The IR absorption band near 500 cm^{-1} is assigned to the M–N stretching frequency in $M(NH_3)_5(N_2)^{2+}$ even though it may couple with other metal–ligand stretching modes. Moreover, the dissociation energy of the M–N bond in the Os complex is larger than that in the Ru one. These facts show that the M–N bond in the former is stronger than that of the latter.

[25] (a) S. I. Zones, T. M. Vickrey, J. B. Palmer, and G. N. Schrauzer, *J. Am. Chem. Soc.*, **98**, 7289 (1976); (b) S. I. Zones, M. L. Palmer, J. G. Palmer, J. M. Doemey, and G. N. Schrauzer, *ibid.*, **100**, 2133 (1978).

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Group 6 Transition-Metal Complexes of Two Macrocycles Containing Tertiary-Phosphino and -Amino Ligating Sites[1]

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Group 6 transition-metal carbonyl complexes of the macrocyclic ligands *cis*-2,10-diphenyl-6-phenyl-6-aza-2,10-diphosphabicyclo[9.4.0]pentadeca-1(11),12,14-triene (**1**, 11-P_2NPh) and *cis*-2,10-diphenyl-6-methyl-6-aza-2,10-diphosphabicyclo[9.4.0]pentadeca-1(11),12,14-triene (**2**, 11-P_2NMe) have been synthesized from the metal hexacarbonyls and the macrocycles by thermolysis. Ligand **1** gives only the tetracarbonyl, whereas **2** yields the *fac*-tricarbonyl via the corresponding tetracarbonyl species. The complexes have been characterized by using ^{1}H, ^{13}C, and ^{31}P NMR, as well as IR spectroscopy.

The synthesis and chemistry of phosphine complexes of the group 6 transition-metal carbonyls have received considerable attention over the years, as indicated by several reviews.[2] We recently described the synthesis and structure of a number of

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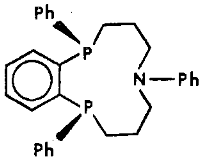
Table I. Carbonyl Stretching Frequencies (cm^{-1}) of Metal Complexes **1**·M(CO)$_4$ and **2**·M(CO)$_3$^{a}

1	Cr	2008 (m), 1927 (m), 1902 (s)
	Mo	2113 (m), 1933 (m), 1912 (s)
	W	2113 (m), 1926 (m), 1903 (s)
2	Cr	1921 (m), 1820 (s), 1810 (s)
	Mo	1932 (m), 1837 (s), 1813 (s)
	W	1922 (m), 1822 (s), 1806 (s)

^{a} Spectra were recorded on 0.7% v/v solutions. The **1**·M(CO)$_4$ series was determined in toluene, which allowed resolution of the $(A_1)_1$ and B_1 bands.[14] No solvent tried resolved the B_1 and B_2 bands. Dichloromethane solutions of **2**·M(CO)$_3$ allowed the resolution of the $(A')_2$ and A'' bands,[14] whereas toluene and other hydrocarbons did not.

tridentate 11-membered rings, including **1** (11-P$_2$NPh) and **2** (11-P$_2$NMe),[1,3] and now report the ligating properties of these species toward the group 6 transition-metal carbonyls, along with spectroscopic properties of the complexes.



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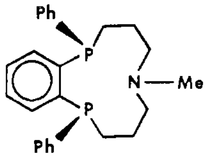

2

Experimental Section

General Data. Melting points were obtained by using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Chemalytics, Inc., Tempe, AZ.

Infrared spectra (IR) were recorded on Perkin-Elmer 237B or Beckman IR9 grating spectrophotometers.

Proton magnetic resonance spectra (^{1}H NMR) were obtained on Perkin-Elmer R-12, Varian A-60, and Varian HA-100 instruments. Chemical shifts are given as parts per million (ppm) downfield from tetramethylsilane (Me$_4$Si) in δ units, and coupling constants are reported in hertz. Multiplicities are given as s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Carbon-13 and phosphorus-31 NMR spectra were determined on a Bruker instrument at 22.6 and 36.4 MHz, respectively. Chemical shifts are given as parts per million (ppm) relative to Me$_4$Si for ^{13}C NMR and relative to 85% H$_3$PO$_4$ for ^{31}P NMR spectra. Chemical shifts upfield from 85% H$_3$PO$_4$ are defined as negative for the ^{31}P spectra. The ^{13}C and ^{31}P NMR spectra are proton decoupled.

The complexation reactions were carried out under reasonably standard conditions so that a detailed experimental description is given only for **1**·Cr(CO)$_4$. Spectroscopic properties of the six complexes described below are summarized in Tables I–III. In every case, analytical samples were prepared by recrystallization from toluene or toluene–hexane and shown by ^{1}H NMR to contain toluene of crystallization (singlet at δ 2.34).

***cis*-Tetrakis(carbonyl-κ*C*){*cis*-2,10-diphenyl-6-phenyl-6-aza-2,10-diphospha-κ^2P-bicyclo[9.4.0]pentadeca-1(11),12,14-triene}chromium(0) [1·Cr(CO)$_4$].** Macrocycle **1** (146 mg, 0.313 mmol) and chromium hexacarbonyl (74 mg, 0.34 mmol) in argon-flushed mesitylene (21 mL) were heated at reflux (165 °C) for 40 min. At this point the IR absorption at 1980 cm^{-1} was essentially zero, and by TLC (SiO$_2$, EtOAc/CH$_2$Cl$_2$/*n*-C$_6$H$_{14}$, 1:1:8, v/v/v), **1** (R_f = 0.50) was absent, and only a single new component was present at R_f = 0.30. The resulting solution was concentrated to dryness on a rotary evaporator and the residue dissolved in hot toluene–hexane (4 mL; 1:1, v/v). The solution, upon being cooled to room temperature, deposited white crystals of **1**·Cr(CO)$_4$ (68 mg, 35%), mp 257–260 °C dec. The ^{1}H NMR spectrum exhibited, in addition to complex absorptions in the δ 7.8–6.4 and 3.6–1.5 region, a sharp singlet at δ 2.34, indicating the presence of approximately 0.5 equiv of toluene (by integration).

Table II. Selected ^{1}H and ^{31}P NMR Chemical Shifts for Complexes **1**·M(CO)$_4$ and **2**·M(CO)$_3$^{a}

	M	δ_P $(\Delta_P)^b$	δ_{NMe} $(\Delta_{NMe})^c$
1	Cr	80.2 (110.3)	
	Mo	57.8 (87.9)	
	W	43.1^d (73.2)	
2	Cr	78.7 (105.9)	2.72 (0.53)
	Mo	56.4 (83.6)	2.75 (0.56)
	W	46.9^e (74.1)	2.97 (0.78)

^{a} Spectra were run on ca. 0.05 M solutions in CD$_2$Cl$_2$. The ^{31}P NMR spectra were proton decoupled, and chemical shifts are defined as positive downfield from external 85% H$_3$PO$_4$. ^{b} Coordination chemical shift: $\Delta_P = \delta_P(\text{complex}) - \delta_P(\text{free})$. $\delta_P(\mathbf{1}) = 30.1$, and $\delta_P(\mathbf{2}) = -27.2$.[1] ^{c} Coordination chemical shift: $\Delta_{NMe} = \delta_H(\text{complex}) - \delta(\text{free})$. $\delta_{NMe} = 2.19$.[1] ^{d} $J_{W-P} = 233$ Hz. ^{e} $J_{W-P} = 230$ Hz.

Anal. Calcd for C$_{34}$H$_{31}$CrNO$_4$P$_2$: C, 64.66; H, 4.95. Calcd for C$_{34}$H$_{31}$CrNO$_4$P$_2$·0.5C$_7$H$_8$: C, 66.3; H, 5.2. Found: C, 66.19; H, 5.46.

***cis*-Tetrakis(carbonyl-κ*C*){*cis*-2,10-diphenyl-6-phenyl-6-aza-2,10-diphospha-κ^2P-bicyclo[9.4.0]pentadeca-1(11),12,14-triene}molybdenum(0) [1·Mo(CO)$_4$].** Macrocycle **1** (122 mg, 0.261 mmol) and molybdenum hexacarbonyl (71 mg, 0.27 mmol) in argon-flushed toluene (20 mL) were boiled under reflux for 1 h, at which point IR and TLC showed the starting materials to be consumed. Workup similar to that for the chromium derivative gave **1**·Mo(CO)$_4$ as white crystals (122 mg, 70%), mp 158–163 °C dec.

Anal. Calcd for C$_{34}$H$_{31}$MoNO$_4$P$_2$: C, 60.45; H, 4.63. Calcd for C$_{34}$H$_{31}$MoNO$_4$P$_2$·0.7C$_7$H$_8$: C, 62.4; H, 5.1. Found: C, 62.52; H, 5.02.

***cis*-Tetrakis(carbonyl-κ*C*){*cis*-2,10-diphenyl-6-phenyl-6-aza-2,10-diphospha-κ^2P-bicyclo[9.4.0]pentadeca-1(11),12,14-triene}tungsten(0) [1·W(CO)$_4$].** Reaction of **1** (146 mg, 0.313 mmol) and tungsten hexacarbonyl (115 mg, 0.33 mmol) in mesitylene (21 mL) as described for the chromium derivative gave **1**·W(CO)$_4$ as white crystals (129 mg, 56%), mp 220–225 °C dec.

Anal. Calcd for C$_{34}$H$_{31}$NO$_4$P$_2$W: C, 53.49; H, 4.39. Calcd for C$_{34}$H$_{31}$NO$_4$P$_2$W·0.5C$_7$H$_8$: C, 55.5; H, 4.4. Found: C, 55.32; H, 4.40.

***fac*-Tris(carbonyl-κ*C*){*cis*-2,10-diphenyl-6-methyl-6-aza-κ*N*-2,10-diphospha-κ^2P-bicyclo[9.4.0]pentadeca-1(11),12,14-triene}chromium(0) [2·Cr(CO)$_3$].** Macrocycle **2** (197 mg, 0.486 mmol) and chromium hexacarbonyl (113 mg, 0.514 mmol) in argon-flushed mesitylene (30 mL) were heated at reflux for 2.6 h. The reaction mixture was cooled to room temperature to give **2**·Cr(CO)$_3$ as orange prisms (97 mg, 37%), mp 285–290 °C dec, which were recrystallized from toluene (83 mg, 32%).

Anal. Calcd for C$_{28}$H$_{29}$CrNO$_3$P$_2$: C, 62.11; H, 5.40. Calcd for C$_{28}$H$_{29}$CrNO$_3$P$_2$·0.6C$_7$H$_8$: C, 64.6; H, 5.6. Found: C, 64.77; H, 5.74.

***fac*-Tris(carbonyl-κ*C*){*cis*-2,10-diphenyl-6-methyl-6-aza-κ*N*-2,10-diphospha-κ^2P-bicyclo[9.4.0]pentadeca-1(11),12,14-triene}molybdenum(0) [2·Mo(CO)$_3$].** Macrocycle **1** (203 mg, 0.502 mmol) and molybdenum hexacarbonyl (137 mg, 0.519 mmol) in argon-flushed toluene (35 mL) were heated at reflux for 2 h. The filtered solution was allowed to cool to room temperature to give **2**·Mo(CO)$_3$ as yellow crystals (177 mg, 60%), mp 220–225 °C dec.

Anal. Calcd for C$_{28}$H$_{29}$MoNO$_3$P$_2$: C, 57.44; H, 4.99. Calcd for C$_{28}$H$_{29}$MoNO$_3$P$_2$·0.5C$_7$H$_8$: C, 59.7; H, 5.3. Found: C, 59.72; H, 5.38.

***fac*-Tris(carbonyl-κ*C*){*cis*-2,10-diphenyl-6-methyl-6-aza-κ*N*-2,10-diphospha-κ^2P-bicyclo[9.4.0]pentadeca-1(11),12,14-triene}tungsten(0) [2·W(CO)$_3$].** Macrocycle **1** (190 mg, 0.470 mmol) and tungsten hexacarbonyl (168 mg, 0.48 mmol) were heated at reflux in argon-flushed mesitylene (30 mL) for 5 h. The filtered solution was cooled to room temperature to give **2**·W(CO)$_3$ as yellow prisms (130 mg, 41%) which were recrystallized from toluene (110 mg, 35%); mp 320–330 °C dec.

Anal. Calcd for C$_{28}$H$_{29}$NO$_3$P$_2$W: C, 49.94; H, 4.34. Calcd for C$_{28}$H$_{29}$NO$_3$P$_2$W·0.6C$_7$H$_8$: C, 52.8; H, 4.7. Found: C, 52.63; H, 4.89.

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(1) Part 4 of the series "Phosphino Macrocycles". For part 3 see: Kyba, E. P.; Davis, R. E.; et al. *J. Am. Chem. Soc.* **1980**, *102*, 139.

(2) (a) Stelzer, O. *Top. Phosphorus Chem.* **1977**, *9*, 1. (b) Chou, K. K.; Leveson, W.; McAuliffe, C. A. In "Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands"; McAuliffe, C. A., Ed.; Halsted Press: New York, 1973; pp 35–204. (c) King, R. B. *Acc. Chem. Res.* **1972**, *5*, 177. (d) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 930. (e) Angelici, R. J. *Organomet. Chem. Rev.* **1968**, *3*, 173.

(3) The systematic names for **1** and **2** reported in ref 1 are rather cumbersome, and for convenience we use the indicated abbreviations. The stereochemistry in **1** and **2** has been established as indicated by single-crystal X-ray diffraction.[1] The systematic names of the complexes used in the experimental section are based on the nomenclature system proposed recently: Sloan, T. E.; Busch, D. E. *Inorg. Chem.* **1978**, *17*, 2043.

Table III. Selected ^{13}C NMR Chemical Shifts and Carbon–Phosphorus Coupling Constants for Complexes 1·M(CO)$_4$ and 2·M(CO)$_3$[a]

	M	δ_{C3} (m)[b] (Δ_{C3})[c]	δ_{NMe} (Δ_{NMe})[c]	δ_{C1} (m)[b] (Δ_{C1})[c]	δ_{C2} (m)[b] (Δ_{C2})[c]
1	Cr	51.4 (s) (−1.8)		30.0 (t, 7.4) (2.8)	24.3 (s) (−1.3)
	Mo	50.6 (s) (−2.6)		29.9 (t, 7.4) (2.7)	24.3 (s) (−1.3)
	W	50.7 (s) (−2.5)		30.4 (d, 20.6) (3.2)	24.5 (s) (−1.1)
2	Cr	65.4 (br s) (10.6)	60.1 (s) (19.3)	28.7 (t, 6.7) (3.1)	21.9 (br s) (−2.7)
	Mo	65.1 (t, 3.0) (10.3)	60.3 (s) (20.1)	29.2 (t, 8.1) (3.6)	22.8 (t, 4.4) (−1.8)
	W	66.0 (d, 7.3) (11.2)	62.9 (s) (22.1)	28.8 (d, 19.2)[d] (3.2)	23.7 (d, 8.9) (−0.9)

[a] Carbon atoms are defined as P–C1–C2–C3–N. Spectra were run on 0.05 M CD_2Cl_2 solutions, and chemical shifts are relative to internal Me_4Si. [b] Multiplicity (m): s = singlet, br = broad, d = doublet, t = triplet. The number following the multiplicity is the coupling constant in hertz. [c] Coordination chemical shift: $\Delta_i = \delta(\text{complex}) - \delta(\text{free})$. The chemical shifts and coupling constants of the free macrocycles are as follows.[1] 1: C3, 53.2 (t, 5 Hz); C1, 27.2 (t, 6 Hz); C2, 25.6 (t, 8 Hz). 2: C3, 54.8 (t, 5 Hz); NMe, 40.8 (s); C1, 25.6 (t, 5 Hz); C2, 24.6 (t, 9 Hz). [d] Upfield absorption of the doublet is a doublet, J = 3.0 Hz.

Results and Discussion

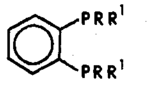
Thermal complexation reactions were carried out with molar equivalents of the macrocycle and metal hexacarbonyl in a boiling aromatic solvent [toluene, Mo(CO)$_6$; mesitylene, Cr(CO)$_6$ and W(CO)$_6$]. The progress of each reaction was monitored by IR spectroscopy in the range 2100–1800 cm^{-1} and thin-layer chromatography (TLC) on silica gel. Equations 1 and 2 illustrate the reactions observed. Isolation of the

$$1 + M(CO)_6 \xrightarrow{\Delta} 1\cdot M(CO)_4 \tag{1}$$

$$2 + M(CO)_6 \xrightarrow{\Delta} 2\cdot M(CO)_4 \rightarrow 2\cdot M(CO)_3 \tag{2}$$

complexes 1·M(CO)$_4$ was effected by rotary evaporation of the solvent to dryness with mesitylene or to about 1 mL/100 mg of starting 1 with toluene. The residue (in the mesitylene reaction) was dissolved in toluene (1 mL/100 mg of starting 1) and filtered, and 1.5 volumes of hexane was added. Crystallization at room temperature gave the colorless tetracarbonyl complexes in 35–70% yields. The yellow tricarbonyl complexes 2·M(CO)$_3$ were much less soluble than the tetracarbonyls and crystallized in yields of 35–60% from the reaction mixture upon cooling to room temperature. All of the complexes isolated incorporated 0.5–0.7 equiv of toluene as evidenced by ^{1}H NMR spectroscopy and elemental analysis.

Not surprisingly, we found no evidence of an intermediate (monophosphine)metal pentacarbonyl species, since no absorption in the 2075–2060-cm^{-1} range[4] was observed during the course of any of the reactions summarized in eq 1 and 2. It is known that the chelation process is highly favored for diphos[5a] and is presumably even more so with the *o*-diphosphino moiety, in which the displacement of the second carbonyl ligand may well be assisted by the proximate uncoordinated phosphine.[1d,e,5] The contrast in reactivity of 1 and 2 at the nitrogen atom leaves little doubt that the third coordination to give 2·M(CO)$_3$ is an assisted process. It is quite unlikely that the activation energies for the dissociative loss of CO from 1·M(CO)$_4$ and 2·M(CO)$_4$ would be very different for any particular metal. Yet, for example, 1·Mo(CO)$_4$ survives under conditions in which 2·Mo(CO)$_4$ is completely destroyed, giving mainly 2·Mo(CO)$_3$. Thus the presence of the much more nucleophilic trialkylamine in 2·M(CO)$_4$ greatly facilitates tricoordination relative to the dialkylaniline in 1·M(CO)$_4$. In fact, we have been unsuccessful in involving the anilino site in 1 in metal complexation even under photochemical conditions, which destroy 1·M(CO)$_4$ to give intractable materials.[6]



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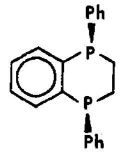

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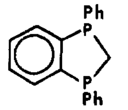

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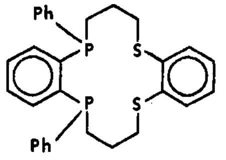

6

Ligands 1 and 2 are formally analogous to species such as 3, which to our knowledge are rather rare. Thus **3a** (R, R^1 = Ph), **3b** (R, R^1 = Me), and **3c** (R, R^1 = Et) are known,[7] but the only diphosphines in which R = phenyl and R^1 = alkyl which have been reported are 4 and 5.[8] There are few metal complexation studies extant dealing with ligands of types 3–5[9] and apparently none dealing with group 6 metal carbonyls. Although we have no X-ray structural information concerning 1·M(CO)$_4$ and 2·M(CO)$_4$, we do have in hand a single-crystal X-ray structure of 6·Mo(CO)$_4$,[10,11] which exhibits a somewhat distorted octahedral coordination about Mo, with a P–Mo–P bond angle of 79°. The IR spectrum of 1·Mo(CO)$_4$ is virtually indistinguishable from that of 6·Mo(CO)$_4$ in the 2100–1800-cm^{-1} region (see Table I), indicating similar coordination about the molybdenum atom in both complexes. Examination of Dreiding and CPK models of 2 reveals that its cavity is too small to enclose a transition metal and that only the *fac*-tridentate bonding arrangement is possible. The IR spectra of 2·M(CO)$_3$ (Table I) are consistent with this ligand arrangement, and in fact we have confirmed the *fac*-tridentate ligation in the case of 2·Mo(CO)$_3$, by a single-crystal X-ray structure determination.[12] The structure is somewhat similar to that of [(Ph$_2$PCH$_2$CH$_2$)$_2$NEt]Cr(CO)$_3$ which has been described[13] as a distorted octahedron with an "astonishingly long" Cr–N bond. Similarly, we find a very long Mo–N bond (2.44 Å), which is essentially the same length as the Mo–P bonds in the complex.[12] The presence of the weak, σ-donor ligand manifests itself in the IR stretching frequencies of the metal carbonyl

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(7) (a) Hart, F. A. *J. Chem. Soc.* **1960**, 3324. (b) Warren, L. F.; Bennett, M. A. *J. Am. Chem. Soc.* **1974**, *96*, 3340.

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(9) For an interesting account of some of the complexation chemistry of **3b**, see ref 7b. Two recent major reviews[2a,b] of phosphine complexes of transition metals do not discuss 3.

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(11) For a description of the synthesis of 6, see: Kyba, E. P.; Hudson, C. W.; McPhaul, M. J.; John, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 8053.

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groups (Table I), in which both the A and E bands are shifted to low frequency, as expected.[14]

Tables II and III summarize pertinent NMR spectroscopic data concerning the six metal carbonyl complexes isolated in this work. The ^{31}P chemical shifts of the complexes are very similar to those reported for diphos derivatives,[15] but the coordination shifts are the largest reported in such complexes. The cause of the large downfield shift in five-membered chelate rings has been suggested to be ring strain,[5c] but subsequent work indicates a more complex situation.[15] The especially large downfield shifts observed in the present work apparently stem from the shielding effect of an *o*-phosphino moiety in the free ligand. Generally, diphenylalkylphosphines exhibit ^{31}P NMR resonance at about −17 ppm[16] (when alkyl ≠ Me, Et), whereas ligands **1** and **2** absorb at −30.1 and −27.2 ppm, respectively. Thus the *o*-phosphino group is shielding by about 10–13 ppm in the *o*-phenylene system, as well as in olefinic systems.[17] Grim has shown that his group contributions to ^{31}P chemical shifts of free phosphines also hold for $(R_3P)M(CO)_5$ species. Although there are currently insufficient data in the literature to be conclusive, the coordination chemical shifts exhibited by the chelated ligands $Me_2PCH_2CH_2PMe_2$[5c] and $(neopentyl)_2PCH_2CH_2P(neopentyl)_2$[20] in $(R_2PCH_2CH_2PR_2)M(CO)_4$ indicate that group contributions derived by Grim[16] also apply in such chelated tetracarbonyls. The especially large coordination chemical shifts for **1**·$M(CO)_4$ and also **2**·$M(CO)_3$ can be accounted for if it is assumed that the shielding effect of the *o*-phosphino group becomes inoperative upon coordination, although clearly more data are needed to clarify this point.[21] Finally, it is interesting to note in the ^1H NMR spectra of the **2**·$M(CO)_3$ complexes that the largest Δ_{NMe} occurs with W, although one might expect the largest change between Cr and Mo, on the basis of the covalent radii of the three metals.

There is a paucity of information with which to compare the ^{13}C NMR data in Table III. The carbon atoms α to coordinated phosphine (C1) experience a deshielding effect of about 3 ppm, whereas the central methylene carbon atoms (C2) are shielded in all six complexes. This latter shielding appears to be approximately constant in **1** but decreases in **2** from Cr to W. In **1**·$M(CO)_4$, the carbon atoms α to nitrogen (C3) are also shielded by about double the amount that C2 atoms are shielded. Finally, coordination of the nitrogen atom in **2**·$M(CO)_3$ results in very large deshielding effects of about 10 ppm for C3 and 20 ppm for NCH_3. Indicative of substantial positive charge on nitrogen in these complexes is the observation that these shifts are similar to those obtained upon N-oxidation of a tertiary amine. For example, N-oxidation of *N*-methylpiperidine results in a downfield shift of 9.4 and 12.7 ppm for C2 and NCH_3, respectively, and upfield shifts of 5.1 and 2.6 ppm for C3 and C4,[22] respectively.

The two- and three-bond carbon–phosphorus coupling constants are reduced essentially to zero upon metal complexation with **1**, whereas C1 exhibits a triplet with a slightly larger one-bond coupling constant in the complex (Cr and Mo) than in the free ligand. With tungsten a considerably larger $^1J_{C-P}$ is observed and apparently the stringent requirements for virtual coupling[23] are not met in **1**·$W(CO)_4$, since the C1 absorption is a doublet. With the tricoordinating ligand **2**, carbon–phosphorus coupling occurs with all three carbon atoms (C1–C3), although with Cr, the coupling is so small for C3 and C2 that only peak broadening is observed. The magnitude of the coupling constant increases from Cr to W for all three carbon atoms, and as for the **1** complexes, virtual coupling does not occur with the tungsten complex.

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Registry No. **1**·$Cr(CO)_4$, 73636-55-2; **1**·$Mo(CO)_4$, 73636-56-3; **1**·$W(CO)_4$, 73636-57-4; **2**·$Cr(CO)_3$, 73636-58-5; **2**·$Mo(CO)_3$, 73636-59-6; **2**·$W(CO)_3$, 73636-60-9; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0.

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(17) Consider the following: δ_P $(Ph_2PCH{=}CH_2)$ −11.7;[16] $(E\text{-}Ph_2PCH{=}CHPPh_2)$ −7.9;[18] $(Z\text{-}Ph_2PCH{=}CHPPh_2)$ −23.1 ppm.[10] Thus substitution in diphenylvinylphosphine for the *E*-H by PPh_2 is deshielding (+4 ppm) whereas the corresponding replacement of the *Z*-H is *shielding* (−12 ppm).

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(21) Relative to chelating diphos[15] and in the absence of the shielding effect of the *o*-phosphino group, one would predict that chelated **1** should be about 4 ppm shielded, because of the difference in contribution of an ethyl (actually CH_2CH_2P) group in diphos and a propyl (actually $CH_2CH_2CH_2N$) group in **1**. In fact, relative to the corresponding diphos complexes, **1**·$M(CO)_4$ complexes are deshielded: M = Cr, 1 ppm; M = Mo, 3 ppm; M = W, 3 ppm.

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Axial Ligand Substitution Reactions of Iron(II) Phthalocyanine Adducts

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Kinetic studies of the ligand substitution reactions of six-coordinate iron(II) phthalocyanine adducts are reported: (T)FePc(L) + X → (T)FePc(X) + L. The T, L, and X ligands include nitrogen and phosphorus donors. The reaction mechanism is strictly dissociative (D). The five-coordinate intermediate, (T)FePc, is extremely reactive and possesses little or no ability to discriminate between nucleophiles. Axial ligand labilities, leaving group effects, trans group effects, and discrimination ratios are discussed and compared to available information on iron porphyrins.

Introduction

Phthalocyanine complexes have been studied for many years because of their value as pigments. More recently the similarity of iron(II) phthalocyanine (FePc) and its bis adducts to iron(II) porphyrins has prompted additional investigations. Kinetic studies of ligand substitution, reaction 1, have been

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