

Table VIII. Selected Mean Torsional Angles (deg)

compd	mean O-Pd-Pd-N
[Pd ₂ (chp) ₄].CHCl ₃ (1)	0.4 [3]
[Pd ₂ (chp) ₄] (2)	6 [1]
[Pd ₂ (chp) ₄].0.5CHCl ₃ (3a) ^a	5 [1]
[Pd ₂ (chp) ₄].0.5CHCl ₃ (3b) ^a	0.2 [8]
<i>trans</i> -[Pd ₂ (mhp) ₄] (4a)	-11 [2]
<i>trans</i> -[Pd ₂ (mhp) ₄] (4b)	0 [1]
<i>cis</i> -[Pd ₂ (mhp) ₄] (4c)	2.92 [6]

^aCrystallographically independent molecules in the same crystal lattice.

or Cl atoms is achieved. Additionally, it should be noted that the torsional angles in compounds 3 and 4 are different for each of the two independent, but otherwise identical, molecules in the respective cells. These differences can probably be attributed to relief of intermolecular strain arising from crystal-packing forces. This type of behavior was observed in one other case,⁹ however,

with only one example it was not clear whether this was unusual or not. We can now ascertain that this type of behavior is not unusual and should be expected in the future.

In closing, we note again that the *cisoid* molecule of [Pd₂(mhp)₄] in compound 4 is the first observed example of a *cisoid* (C_{2h}) isomer of an [M₂(xhp)₄] molecule, although a few other *cisoid* [M₂(XYZ)₄] type molecules with other bridging ligands have been observed.²

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Supplementary Material Available: Tables of bond distances, bond angles, anisotropic thermal parameters, torsional angles, and observed and calculated structure factors (102 pages). Ordering information is given on any current masthead page.

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Reactions of Small Molecules with Re₂Cl₄(PEt₃)₄. 1. Structural and Spectroscopic Studies of Several Products Resulting from the Reaction with Carbon Monoxide

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The reaction of carbon monoxide at about 120 atm pressure with Re₂Cl₄(PEt₃)₄ in dichloromethane solution has been found to yield several products. The structures of four of them, *all-trans*-Re(CO)₂Cl₂(PEt₃)₂ (1), *mer*-Re(CO)₃Cl(PEt₃)₂ (2), *cis*-Re(CO)₄Cl(PEt₃) (3), and *trans*-ReCl₄(PEt₃)₂ (4), have been determined by single-crystal X-ray diffraction methods. The structure of the dicarbonyl compound is the first reported for the general class of 17-electron Re(II) compounds Re(CO)₂X₂(PR₃)₂. Infrared spectra were measured and Cotton-Kraihanzel calculations carried out on the carbonyl compounds. The combined structural and spectroscopic results are shown to exhibit the correlations expected for low-valent rhenium carbonyls. The salient data for each compound are as follows. 1: IR 1912 cm⁻¹; space group P2₁/c; unit cell *a* = 7.521 (1) Å, *b* = 10.853 (1) Å, *c* = 14.853 (2) Å, β = 118.25 (4)°, *V* = 1068 (1) Å³, *Z* = 2. 2: IR 2045, 1887, 1940 cm⁻¹; space group P1; unit cell *a* = 7.971 (1) Å, *b* = 9.107 (2) Å, *c* = 7.624 (2) Å, α = 95.25 (1)°, β = 92.23 (2)°, γ = 107.68 (1)°, *V* = 523.9 (3) Å³, *Z* = 1. 3: IR 2102, 1997, 1987, 1942 cm⁻¹; space group P2₁/n; unit cell *a* = 6.422 (1) Å, *b* = 14.761 (1) Å, *c* = 15.778 (2) Å, β = 94.80 (2)°, *V* = 1490.4 (6) Å³, *Z* = 4. 4: space group P1; unit cell *a* = 8.395 (8) Å, *b* = 8.698 (6) Å, *c* = 7.508 (7) Å, α = 96.19 (4)°, β = 93.04 (2)°, γ = 71.54 (3)°, *V* = 516.8 (6) Å³, *Z* = 1. The infrared spectra and CO stretching force constants are shown to correlate with the structures.

Introduction

It is now well-known that the reactions of π-acid ligands such as carbon monoxide, nitric oxide, and isocyanides with compounds containing triply and quadruply bonded dimetal cores characteristically afford products in which metal-metal bond rupture has occurred,^{2a} although in special cases bond retention occurs.^{2b} Not infrequently reduction accompanies this bond scission.³ We have undertaken a detailed study of the reactions of small molecules with the dimer Re₂Cl₄(PEt₃)₄ and have found that several products are formed in the reaction of this species with CO. Walton and co-workers have already pioneered the study of the reactions of CO with Re₂X₄(PR₃)₄ compounds,^{4,5} but their work

employed CO at atmospheric pressure only, whereas in this research we have carried out reactions with CO at pressures of about 120 atm. This has led to differences in product distribution, favoring higher CO content and more reduction.

We have used single-crystal X-ray diffraction methods to determine the structures of four of the compounds produced in the reaction of CO with the title compound, namely *all-trans*-Re(CO)₂Cl₂(PEt₃)₂ (1), *mer*-Re(CO)₃Cl(PEt₃)₂ (2), *cis*-Re(CO)₄Cl(PEt₃) (3), and *trans*-ReCl₄(PEt₃)₂ (4). The structure of the 17-electron dicarbonyl (a member of a class of compounds first reported by Walton and co-workers⁴) is the first one reported for a compound of the general formula Re(CO)₂X₂(PR₃)₂. The structure determination for *mer*-Re(CO)₃(PEt₃)₂Cl (2) entailed the resolution of a disorder between a Cl and a CO ligand. The molecule *trans*-ReCl₄(PEt₃)₂ (4) was found to be similar to ReCl₄(PMe₂Ph)₂, previously described by Mason and co-workers.⁶

The infrared spectra in the carbonyl stretching region have been measured for 1, 2, and 3, and force constant (Cotton-Kraihanzel) calculations⁷ have been carried out. For *cis*-Re(CO)₄(PEt₃)Cl, which possesses local C_s symmetry, a secular equation not reported

- (1) (a) Southern Illinois University. (b) Texas A&M University.
 (2) (a) Walton, R. A. *ACS Symp. Ser.* **1981**, No. 155, 212-217. (b) Cotton, F. A.; Daniels, L. M.; Dunbar, K. R.; Falvello, L. R.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1985**, *107*, 3524.
 (3) In this article we shall be referring only to the M-M bonds in the high-valent metal cluster compounds (HVC's). In the low-valent clusters (LVC's) the presence of π-acceptor ligands, for example CO in Cp(CO)₂Mo=Mo(CO)₂Cp, is commonplace because the metal atoms have 18-electron configurations and, hence, can supply electrons both to M-M multiple bonds and to M-CO π bonds simultaneously. For a discussion of this, see: Cotton, F. A. *ACS Symp. Ser.* **1983**, No. 211, 209-219.
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 (6) Aslanov, L.; Mason, R.; Wheeler, A. G.; Whimp, P. O. *J. Chem. Soc., Chem. Commun.* **1970**, 30.
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 Cotton, F. A. *Inorg. Chem.* **1964**, *3*, 702.

in previous papers on the method was generated.

The structural data obtained and their correlation with the computational results will be discussed.

Experimental Section

Preparation of Starting Materials. The high-pressure reactor and cell assembly have been described previously.⁸ The compound $(n\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ was prepared by an established method.⁹ $\text{Re}_2\text{Cl}_4(\text{PET}_3)_4$ was prepared by the sodium borohydride reduction in ethanol of $(n\text{-Bu}_4\text{N})_2[\text{Re}_2\text{Cl}_8]$ in the presence of triethylphosphine¹⁰ and was subsequently recrystallized from dichloromethane/diethyl ether carefully purged of water and oxygen. All solvents were reagent grade or better; preliminary drying was accomplished by the use of molecular sieves. Dichloromethane and acetonitrile were subsequently dried over phosphorus pentoxide and distilled from this agent under a nitrogen atmosphere. *n*-Hexane was dried over sodium wire followed by distillation from sodium benzophenone ketyl under nitrogen. CP grade carbon monoxide (Matheson) was passed over Ascarite, BTS catalyst, and molecular sieves to remove any traces of carbon dioxide, oxygen, and water. CP grade nitrogen (Matheson) was passed over BTS catalyst and molecular sieves.

General Preparative Procedures. All solid and liquid samples were manipulated by Schlenk techniques under a nitrogen atmosphere. Solutions of $\text{Re}_2\text{Cl}_4(\text{PET}_3)_4$ in dichloromethane were transferred by cannula under nitrogen to the reactor system. The reactor was then charged to the desired pressure with carbon monoxide, and the reaction was allowed to proceed with vigorous stirring. The contents of the reactor were transferred to a Schlenk vessel upon completion of a given reaction and the venting of excess carbon monoxide from the reactor.

The components of the reaction mixture were separated by flash chromatography (5 psig of N_2) on a 2.5×20 cm column of 230–400 mesh ASTM silica gel. The column was purged of oxygen prior to the loading of samples.

Crystals suitable for single-crystal X-ray diffraction were obtained by recrystallization from appropriate oxygen-free dehydrated solvents.

Reaction of $\text{Re}_2\text{Cl}_4(\text{PET}_3)_4$ and CO at 27 °C. In a typical reaction, 0.35 g (3.0×10^{-4} mol) of the dimer was dissolved in 15 mL of dichloromethane. The solution was transferred to the reactor system, and the reactor was then charged with 120 atm of CO at 27 °C for a period of 24 h. The reaction mixture was stirred vigorously during the reaction. Upon conclusion of the reaction the CO was vented and the remaining contents of the reactor were transferred to a Schlenk vessel under an atmosphere of nitrogen.

The components of the mixture were separated on a column packed with silica gel suspended in *n*-hexane. The first 300 mL of eluant (2:1 v/v mixture of *n*-hexane/dichloromethane) gave 10.1 mg of the red crystalline compound $\text{trans-ReCl}_4(\text{PET}_3)_2$. A 20.0-mg sample of *all-trans-Re}(\text{CO})_2\text{Cl}_2(\text{PET}_3)_2 was isolated from the next 150 mL of eluant. A 28.8-mg sample of the white crystalline compound *mer-Re}(\text{CO})_3\text{Cl}(\text{PET}_3)_2* was obtained from the next 150 mL of eluant (pure dichloromethane). From the final 120 mL of eluant (pure acetonitrile) was obtained 54.4 mg of the green crystalline compound $\text{Re}_2\text{Cl}_6(\text{PET}_3)_2$.*

For a reaction time of 48 h, all other conditions invariant, four compounds were isolated. A 12.0-mg sample of *trans-ReCl}_4(\text{PET}_3)_2* was obtained from the first 300 mL of eluant (2:1 v/v *n*-hexane/dichloromethane). The second fraction gave 20.0 mg of *all-trans-Re}(\text{CO})_2\text{Cl}_2(\text{PET}_3)_2*, the third fraction gave 120 mg of *mer-Re}(\text{CO})_3\text{Cl}(\text{PET}_3)_2* and trace amounts of $\text{Re}(\text{CO})_4\text{Cl}(\text{PET}_3)$, and the fourth fraction yielded 10.2 mg of a dark green material that could not be crystallized. This product was not fully characterized but is presumed to be an impure sample of $\text{Re}_2\text{Cl}_6(\text{PET}_3)_2$.

Reaction of $\text{Re}_2\text{Cl}_4(\text{PET}_3)_4$ and CO at 55 °C. The experimental procedure for this study was the same as that described for the reaction carried out at 27 °C. For a reaction time of 48 h, the products were isolated in the following yields: *all-trans-Re}(\text{CO})_2\text{Cl}_2(\text{PET}_3)_2*, 7.6 mg; *mer-Re}(\text{CO})_3\text{Cl}(\text{PET}_3)_2*, 150 mg; *cis-Re}(\text{CO})_4\text{Cl}(\text{PET}_3), 70 mg; $\text{Re}(\text{C}(\text{O})_5\text{Cl}$, trace.*

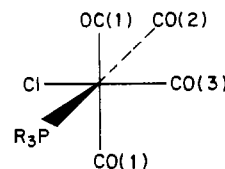
X-ray Crystallography. The methods utilized for data collections and the solution and refinements of the structures were as described in detail previously.¹¹ Crystallographic results are summarized in Tables I–XII.

Infrared Spectra and Force Constants. The infrared spectra in the carbonyl region were measured on cyclohexane solutions with a Perkin-Elmer 283 spectrometer. Force constants were calculated by the Cotton–Kraihanzel method.⁷ The results are displayed in Table XIII. A few words of explanation concerning each calculation will now be given. In all cases an interaction constant k_i between two *cis* CO groups is employed with the assumption that for two *trans* CO groups the interaction constant would be equal to $2k_i$.

For **1**, with only the infrared-active frequency (due to the antisymmetric vibration) known, only the value of $k - 2k_i$ can be directly determined as 14.76 mdyne/Å. In Table XIII we list a value of k together with an assumed value of k_i . The *all-trans-M}(\text{CO})_2\text{X}_2\text{L}_2 molecule has D_{2h} symmetry, and the appropriate secular equations are identical with those previously given⁷ for the *trans-M}(\text{CO})_2\text{L}_4 case.**

For **2**, with C_{2v} symmetry, the secular equations previously given⁷ for *trans-M}(\text{CO})_3\text{L}_3 are applicable, with CO(1) and its force constant k_1 being associated with the unique CO group. The assignment given in Table XIII is based on the following considerations. For a CO *trans* to Cl the force constant should be at least 1.0 mdyne/Å less than that for the CO's that are *trans* to each other. The value of k_i ought to be ca. 0.3–0.5 mdyne/Å. From the secular equations it is unequivocal then that the A_1^2 mode (the symmetric stretch for the pair of *trans* CO groups) must have the highest frequency. It should also be by far the weakest band. The very weak band at 2045 cm^{-1} is thus unambiguously assignable as the A_1^2 band, and it can be estimated that the B_1 mode would be ca. 100 cm^{-1} lower while the A_1^1 mode would have to be still lower. The force constants given reproduce the frequencies to within 1 cm^{-1} .*

For **3**, the necessary secular equations had not been previously given, and we shall derive them for this case, where the effective symmetry is just C_2 and all vibrations are either A' (symmetric to reflection in the mirror plane) or A'' (antisymmetric to reflection). We label the CO's and their associated force constants (k_1 , k_2 , and k_3) as



The two CO(1)'s give rise to an A' and an A'' mode, while CO(2) and CO(3) each generate an A' mode. Thus, the secular equations must consist of one linear equation for the A'' vibration and a cubic equation for the three coupled A' modes. These can be shown, by standard methods,⁷ to be

$$\lambda = \mu(k_1 - 2k_i) = 0$$

$$\begin{vmatrix} (k_1 + 2k_i)\mu - \lambda & 2^{1/2}\mu k_i & 2^{1/2}\mu k_i \\ 2^{1/2}\mu k_i & \mu k_2 - \lambda & \mu k_i \\ 2^{1/2}\mu k_i & \mu k_i & \mu k_3 - \lambda \end{vmatrix} = 0$$

where the symbols have their standard definitions, as previously defined.⁷

Again, assignments follow from our general prior knowledge of these systems. It is expected that $k_1 > k_2 > k_3$, with the difference between k_1 and k_3 well in excess of 1.0 mdyne/Å. Also, k_i should be in the range 0.2–0.4 mdyne/Å. The highest frequency band should be the A' mode arising mainly from the two CO(1) groups, and it should be the weakest band in the spectrum, which was observed to be true. Thus, the assignment and the resulting force constants given in Table XIII are obtained. These force constants reproduce the frequencies to within 1 cm^{-1} .

Results

Structural Results. Since the *all-trans-Re}(\text{CO})_2\text{Cl}_2(\text{PET}_3)_2 structure (compound **1**) is the first of its type to be reported, it will be discussed first. An ORTEP diagram of this molecule is given in Figure 1. Information pertinent to the data collection and refinement of the structure is given in Table I. Positional parameters are listed in Table II, and bond distances and angles are given in Table III. The mutually *trans* disposition of all ligands is immediately obvious. The rhenium atom resides on a crystallographic center of inversion, and the angles about the metal atom are close to those of a regular octahedron. The $\text{ReC}_2\text{Cl}_2\text{P}_2$ core has effectively D_{2h} symmetry. The Re–P distance of 2.470 (4) Å and the Re–Cl and Re–C_{CO} distances (2.407 (4) and 1.980 (17) Å, respectively) are all similar to those in the related Re(I) compounds studied (*vide infra*).*

An ORTEP diagram of the structure of *mer-Re}(\text{CO})_3\text{Cl}(\text{PET}_3)_2 (**2**) is given in Figure 2. Information pertinent to data collection*

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(12) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1980; pp 1199–1202.

Table I. Crystallographic Parameters for *all-trans-Re(CO)₂(PEt₃)₂Cl₂*

formula	$\text{ReCl}_2\text{P}_2\text{O}_2\text{C}_{14}\text{H}_{30}$
fw	549.48
space group	$P2_1/c$
systematic absences	$h0l, l = 2n; 0k0, k = 2n$
<i>a</i> , Å	7.521 (1)
<i>b</i> , Å	10.853 (1)
<i>c</i> , Å	14.853 (2)
β , deg	118.25 (4)
<i>V</i> , Å ³	1068.0 (6)
<i>Z</i>	2
<i>d</i> _{calcd.} , g/cm ³	1.708
cryst size, mm	0.35 × 0.25 × 0.20
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	61.684
data collecn instrument	Syntex P1
radiation (monochromated in incident beam)	Mo K α
orientation reflcns: no.; range (2 θ), deg	15; 27.0 < 2 θ < 43.0
temp, °C	22 ± 1
scan method	θ -2 θ
data collecn range, 2 θ , deg	5.0 < 2 θ < 45.0
no. of unique data, total	1492
no. with $F_o^2 > 3\sigma(F_o^2)$	1180
no. of parameters refined	97
transmission factors: max, min (exptl)	0.994, 0.813
<i>R</i> ^a	0.048
<i>R</i> _w ^b	0.052
quality-of-fit indicator ^c	1.521
largest shift/esd, final cycle	0.01
largest peak, e/Å ³	0.769

^a $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^cQuality of fit = $[\sum w(|F_o| - |F_c|)^2/(N_{\text{observns}} - N_{\text{params}})]^{1/2}$.

Table II. Positional Parameters and Their Equivalent Isotropic Thermal Parameters for *all-trans-Re(CO)₂(PEt₃)₂Cl₂*

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Re(1)	0	0	0	2.82 (3)
Cl(1)	0.2119 (5)	-0.1342 (4)	0.4194 (3)	4.1 (1)
P(1)	0.2745 (5)	0.1772 (4)	0.4183 (3)	3.3 (1)
O(1)	0.418 (2)	0.026 (1)	0.6864 (9)	5.7 (4)
C(1)	0.451 (2)	0.015 (1)	0.619 (1)	3.2 (4)
C(11)	0.380 (2)	0.331 (1)	0.469 (1)	4.7 (5)
C(12)	0.423 (3)	0.351 (2)	0.584 (1)	6.3 (6)
C(21)	0.199 (2)	0.203 (1)	0.282 (1)	4.2 (5)
C(22)	0.073 (2)	0.095 (1)	0.210 (1)	5.2 (5)
C(31)	0.035 (2)	0.169 (2)	0.424 (1)	6.2 (6)
C(32)	-0.116 (2)	0.271 (2)	0.375 (1)	5.6 (6)

^aAnisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

Table III. Bond Distances (Å) and Bond Angles (deg) and Their Esd's for *all-trans-Re(CO)₂(PEt₃)₂Cl₂*

Re(1)-Cl(1)	2.407 (4)	P(1)-C(21)	1.848 (14)
Re(1)-P(1)	2.470 (4)	P(1)-C(31)	1.843 (14)
Re(1)-C(1)	1.980 (17)	C(11)-C(12)	1.601 (20)
C(1)-O(1)	1.141 (19)	C(21)-C(22)	1.563 (20)
P(1)-C(11)	1.847 (15)	C(31)-C(32)	1.508 (21)
Cl(1)-Re(1)-P(1)	88.8 (1)	Re(1)-P(1)-C(21)	116.1 (5)
Cl(1)-Re(1)-C(1)	89.3 (4)	Re(1)-P(1)-C(31)	113.4 (6)
P(1)-Re(1)-C(1)	89.9 (4)	P(1)-C(11)-C(12)	112.8 (1)
Re(1)-C(1)-O(1)	178.1 (12)	P(1)-C(21)-C(22)	114.0 (10)
Re(1)-P(1)-C(11)	116.1 (5)	P(1)-C(31)-C(32)	118.4 (13)

and structural refinement is given in Table IV. Positional parameters are listed in Table V, and bond distances and angles are given in Table VI. The rhenium atom resides on a crystallographic inversion center, and this entails a systematic disordering of one CO group and the chlorine atom trans to it. The distortion of the thermal ellipsoids representing the unique chlorine atom and the carbon and oxygen atoms of the carbonyl ligand trans to the chlorine are a result of this disorder. Refinement of this

Table IV. Crystallographic Parameters for *mer-Re(CO)₃(PEt₃)₂Cl*

formula	$\text{ReClP}_2\text{O}_3\text{C}_{15}\text{H}_{30}$
fw	542.01
space group	$P\bar{1}$
systematic absences	none
<i>a</i> , Å	7.971 (1)
<i>b</i> , Å	9.107 (2)
<i>c</i> , Å	7.624 (2)
α , deg	95.25 (1)
β , deg	92.23 (2)
γ , deg	107.68 (1)
<i>V</i> , Å ³	523.9 (3)
<i>Z</i>	1
<i>d</i> _{calcd.} , g/cm ³	1.718
cryst size, mm	0.35 × 0.20 × 0.20
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	61.645
data collecn instrument	Nicolet P1
radiation (monochromated in incident beam)	Mo K α
orientation reflcns: no.; range (2 θ), deg	25; 20.0 < 2 θ < 45.0
temp, °C	22 ± 1
scan method	θ -2 θ
data collecn range, 2 θ , deg	5.0 < 2 θ < 45.0
no. of unique data, total	2378
no. with $F_o^2 > 3\sigma(F_o^2)$	2373
no. of parameters refined	118 (disordered model)
transmission factors: max, min (exptl)	0.998, 0.842
<i>R</i> ^a	0.024
<i>R</i> _w ^a	0.031
quality-of-fit indicator ^a	1.121
largest shift/esd, final cycle	0.001
largest peak, e/Å ³	0.432

^aSee footnotes to Table I for definitions.

Table V. Positional Parameters and Their Equivalent Isotropic Thermal Parameters for *mer-Re(CO)₃(PEt₃)₂Cl*

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Re(1)	0	0	0	2.464 (5)
Cl(1)	0.0459 (8)	0.813 (2)	0.208 (3)	3.9 (2)
P(1)	0.1153 (1)	0.2186 (1)	0.2255 (1)	2.89 (2)
O(1)	0.6218 (6)	0.9322 (6)	0.1329 (7)	6.2 (1)
C(1)	0.9523 (7)	0.2977 (6)	0.3283 (6)	3.9 (1)
C(1C)	0.7571 (6)	0.9587 (5)	0.0840 (6)	3.7 (1)
C(2)	0.8515 (8)	0.3665 (7)	0.2005 (8)	5.0 (1)
C(3)	0.2310 (6)	0.1841 (6)	0.4237 (6)	3.8 (1)
C(4)	0.4001 (8)	0.1441 (8)	0.3878 (8)	5.3 (1)
C(5)	0.2751 (7)	0.3846 (5)	0.1421 (7)	4.3 (1)
C(6)	0.3465 (9)	0.5323 (6)	0.2712 (9)	5.9 (2)
C	0.046 (2)	-0.155 (8)	0.170 (8)	5.6 (5)
O	0.070 (3)	-0.226 (4)	0.254 (4)	5.0 (4)

^aSee footnote to Table II.

Table VI. Bond Distances (Å) and Bond Angles (deg) and Their Esd's for *mer-Re(CO)₃(PEt₃)₂Cl*

Re(1)-P(1)	2.430 (1)	P(1)-C(5)	1.839 (5)
Re(1)-C(1C)	2.000 (5)	C(1C)-O(1)	1.118 (6)
Re(1)-Cl(1)	2.487 (15)	C(CO)-O(CO)	1.148 (50)
Re(1)-C(CO)	1.922 (1)	C(1)-C(2)	1.532 (7)
P(1)-C(1)	1.835 (4)	C(3)-C(4)	1.528 (7)
P(1)-C(3)	1.840 (4)	C(5)-C(6)	1.533 (7)
P(1)-Re(1)-Cl(1)	91.8 (1)	O(1)-C(1C)-Re(1)	178.1 (4)
C(1C)-Re(1)-Cl(1)	87.3 (2)	Cl(1)-C(CO)-Re(1)	171.2 (9)
C(1C)-Re(1)-P(1)	91.2 (1)	O(CO)-C(CO)-Re(1)	179.4 (17)
C(CO)-Re(1)-P(1)	91.3 (4)	C(CO)-Re(1)-C(1C)	89.2 (5)
O(CO)-Cl(1)-Re(1)	170.0 (16)	C(1)-P(1)-Re(1)	116.3 (2)
C(3)-P(1)-Re(1)	116.2 (7)	C(5)-P(1)-Re(1)	112.5 (2)
C(3)-P(1)-C(1)	100.2 (5)	C(5)-P(1)-C(1)	105.2 (4)
C(5)-P(1)-C(3)	104.4 (2)	C(2)-C(1)-P(1)	114.1 (3)
C(4)-C(3)-P(1)	114.1 (3)	C(6)-C(5)-P(1)	116.5 (4)

disorder model was accomplished by the application of distance restraints in the form of observational equations. This treatment led to a smooth convergence of the structural model, and no further problems were encountered during the refinement. Despite the

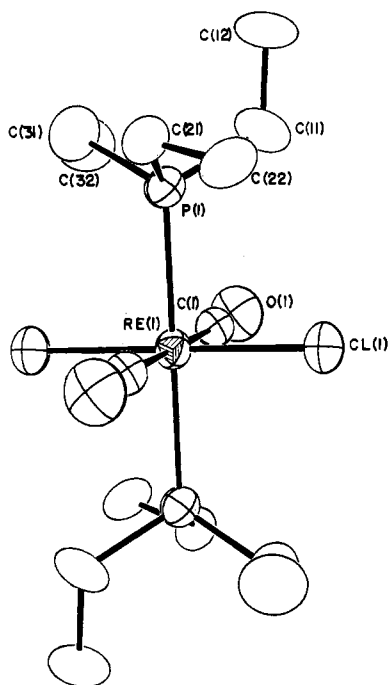


Figure 1. ORTEP diagram of *all-trans*- $\text{Re}(\text{CO})_2(\text{PEt}_3)_2\text{Cl}_2$. Atoms are represented as thermal ellipsoids at the 50% probability level.

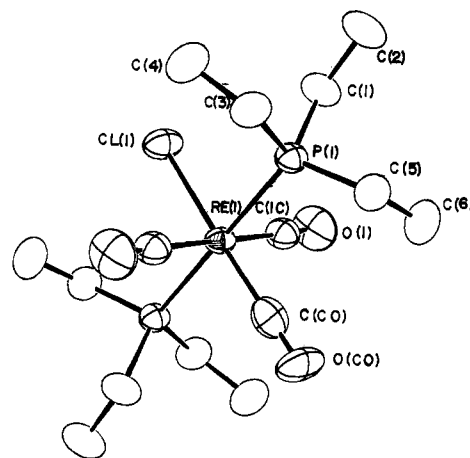


Figure 2. ORTEP diagram of *mer*- $\text{Re}(\text{CO})_3(\text{PEt}_3)_2\text{Cl}$. Atoms are represented as thermal ellipsoids at the 50% probability level.

Table VII. Crystallographic Parameters for *cis*- $\text{Re}(\text{CO})_4(\text{PEt}_3)\text{Cl}$

formula	$\text{ReO}_4\text{PClC}_{10}\text{H}_{15}$
fw	451.86
space group	$P2_1/n$
systematic absences	$h0l, h + l = 2n; 0k0, k = 2n$
$a, \text{\AA}$	6.422 (1)
$b, \text{\AA}$	14.761 (1)
$c, \text{\AA}$	15.778 (2)
β, deg	94.80 (2)
$V, \text{\AA}^3$	1490.4 (6)
Z	4
$d_{\text{calcd}}, \text{g/cm}^3$	2.014
cryst size, mm	$0.35 \times 0.30 \times 0.30$
$\mu(\text{Mo K}\alpha), \text{cm}^{-1}$	85.50
data collect instrument	Syntex P1
radiation (monochromated in incident beam)	$\text{Mo K}\alpha$
orientation reflcns: no.; range (2θ), deg	15; $25.0 < 2\theta < 45.0$
temp, $^\circ\text{C}$	22 ± 1
scan method	$\theta-2\theta$
data collect range, 2θ , deg	$5.0 < 2\theta < 50.0$
no. of unique data, total	1568
no. with $F_o^2 > 3\sigma(F_o^2)$	1320
no. of parameters refined	144
transmission factors: max, min (exptl)	0.995, 0.828
R^a	0.048
R_w^a	0.065
quality-of-fit indicator ^a	1.669
largest shift/esd, final cycle	0.30
largest peak, $\text{e}/\text{\AA}^3$	0.520

^aSee footnotes to Table I for definitions.

disorder the Re–CO and Re–Cl distances are quite accurate and are 1.922 (1) and 2.487 (15) \AA , respectively. Once again, deviations from octahedral angles are minimal. The mutually trans Re–CO distances of 2.000 (5) \AA are very similar to that of the dicarbonyl, viz., 1.980 (17) \AA .

The compound *cis*- $\text{Re}(\text{CO})_4\text{Cl}(\text{PEt}_3)$ (3) is depicted in the ORTEP diagram given in Figure 3. Information pertinent to the data collection and solution and refinement of the structure is given in Table VII. Positional parameters are given in Table VIII, and bond distances and angles are given in Table IX. The entire molecule constitutes the asymmetric unit and thus has no crys-

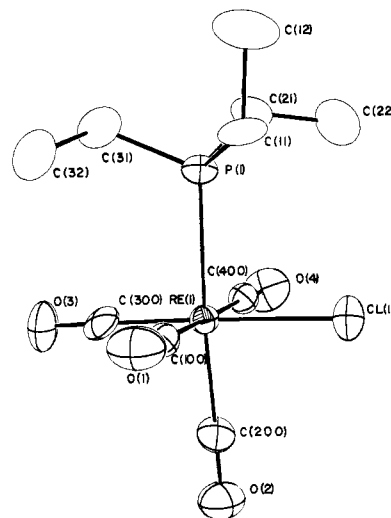


Figure 3. ORTEP diagram of *cis*- $\text{Re}(\text{CO})_4(\text{PEt}_3)\text{Cl}$. Atoms are represented as thermal ellipsoids at the 50% probability level.

Table VIII. Positional Parameters and Their Equivalent Isotropic Thermal Parameters for *cis*- $\text{Re}(\text{CO})_4(\text{PEt}_3)\text{Cl}$

atom	x	y	z	$B, \text{\AA}^2$
Re(1)	0.17895 (8)	0.20235 (4)	0.44463 (3)	2.05 (1)
Cl(1)	-0.1422 (6)	0.2940 (3)	0.4620 (3)	3.41 (9)
P(1)	0.2704 (6)	0.3137 (3)	0.3357 (2)	2.37 (8)
C(100)	0.329 (2)	0.278 (1)	0.5331 (9)	2.5 (3)*
C(200)	0.081 (2)	0.119 (1)	0.5288 (9)	3.2 (3)
C(300)	0.425 (3)	0.130 (1)	0.4348 (9)	3.3 (4)
C(400)	0.022 (2)	0.132 (1)	0.3540 (8)	2.2 (3)*
O(1)	0.409 (2)	0.3210 (9)	0.5873 (7)	4.9 (3)
O(2)	0.029 (2)	0.0699 (9)	0.5787 (7)	4.8 (3)
O(3)	0.578 (2)	0.0884 (8)	0.4329 (7)	4.3 (3)
O(4)	-0.064 (2)	0.0949 (8)	0.2987 (7)	4.7 (3)
C(11)	0.373 (2)	0.425 (1)	0.375 (1)	3.4 (4)
C(12)	0.224 (3)	0.482 (1)	0.420 (1)	5.7 (5)
C(21)	0.045 (2)	0.340 (1)	0.260 (1)	3.5 (4)
C(22)	0.085 (3)	0.411 (1)	0.193 (1)	5.5 (5)
C(31)	0.471 (2)	0.274 (1)	0.270 (1)	3.5 (4)
C(32)	0.418 (3)	0.190 (1)	0.217 (1)	4.4 (5)

^aSee footnote to Table II. Atoms marked with an asterisk were refined isotropically.

tallographically imposed symmetry. However, the molecule has an approximate plane of symmetry (neglecting the ethyl groups) such that the two CO groups perpendicular to the plane (which is defined by the Re, P, and Cl atoms) have identical Re–C distances of 1.973 (13) and 1.976 (12) \AA . The Re–Cl distance of 2.501 (3) \AA is similar to that in $\text{Re}(\text{CO})_5\text{Cl}$ (2.501 (3) \AA).¹³

Table IX. Bond Distances (Å) and Bond Angles (deg) and Their Esd's for *cis*- $\text{Re}(\text{CO})_4(\text{PEt}_3)\text{Cl}$

Re(1)–Cl(1)	2.501 (3)	P(1)–C(11)	1.851 (12)
Re(1)–P(1)	2.484 (3)	P(1)–C(21)	1.839 (12)
Re(1)–C(100)	1.973 (13)	P(1)–C(31)	1.812 (14)
Re(1)–C(200)	1.951 (14)	C(11)–C(12)	1.501 (20)
Re(1)–C(300)	1.922 (16)	C(21)–C(22)	1.536 (18)
Re(1)–C(400)	1.976 (12)	C(31)–C(32)	1.526 (19)
C(100)–O(1)	1.153 (15)	C(200)–O(2)	1.142 (14)
C(300)–O(3)	1.161 (15)	C(400)–O(4)	1.132 (13)
Cl(1)–Re(1)–P(1)	87.86 (11)	C(100)–Re(1)–C(200)	92.30 (50)
Cl(1)–Re(1)–C(100)	88.49 (36)	C(100)–Re(1)–C(300)	90.85 (50)
Cl(1)–Re(1)–C(200)	87.18 (38)	C(100)–Re(1)–C(400)	177.23 (45)
Cl(1)–Re(1)–C(300)	178.22 (35)	C(200)–Re(1)–C(300)	91.19 (52)
Cl(1)–Re(1)–C(400)	89.31 (33)	C(200)–Re(1)–C(400)	89.28 (48)
P(1)–Re(1)–C(100)	89.17 (36)	C(300)–Re(1)–C(400)	91.39 (48)
P(1)–Re(1)–C(200)	174.79 (37)	Re(1)–C(100)–O(1)	178.86 (115)
P(1)–Re(1)–C(300)	93.79 (37)	Re(1)–C(200)–O(2)	178.35 (114)
P(1)–Re(1)–C(400)	89.06 (33)	Re(1)–C(300)–O(3)	176.50 (101)
Re(1)–P(1)–C(11)	116.87 (42)	Re(1)–C(400)–O(4)	175.99 (98)
Re(1)–P(1)–C(21)	111.60 (40)	Re(1)–P(1)–C(31)	113.75 (47)
C(11)–P(1)–C(21)	105.76 (65)	C(11)–P(1)–C(31)	102.92 (62)
C(21)–P(1)–C(31)	104.80 (59)		

Table X. Crystallographic Parameters for *trans*- $\text{ReCl}_4(\text{PEt}_3)_2$

formula	$\text{ReCl}_4\text{P}_2\text{C}_{12}\text{H}_{30}$
fw	564.33
space group	$P\bar{1}$
systematic absences	none
<i>a</i> , Å	8.395 (8)
<i>b</i> , Å	8.698 (6)
<i>c</i> , Å	7.508 (7)
α , deg	96.19 (4)
β , deg	93.04 (2)
γ , deg	71.54 (3)
<i>V</i> , Å ³	516.8 (6)
<i>Z</i>	1
cryst size, mm	0.40 × 0.30 × 0.30
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	66.22
data collec instrument	Syntax P1
radiation (monochromated in incident beam)	Mo K α
orientation reflcns: no.; range (2 θ), deg	15; 5.0 < 2 θ < 35.0
temp, °C	22 ± 1
scan method	θ -2 θ
data collec range, 2 θ , deg	5.0 < 2 θ < 50.0
no. of unique data, total	804
no. with $F_o^2 > 3\sigma(F_o^2)$	765
no. of parameters refined	91
transmission factors: max, min (exptl)	0.999, 0.822
R^a	0.033
R_w^a	0.043
quality-of-fit indicator ^a	0.864
largest shift/esd, final cycle	0.01
largest peak, e/Å ³	0.857

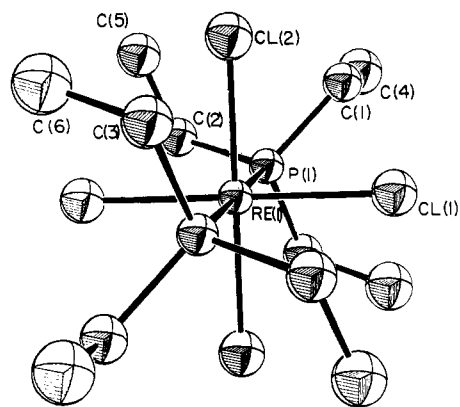
^aSee footnotes to Table I for definitions.

However, the Re–P distance of 2.484 (3) Å is considerably longer than that in the tricarbonyl, viz., 2.430 (1) Å. This may be ascribed to the superiority of the π -acceptor ability of a carbonyl ligand over that of a trialkylphosphine ligand.

The structure of *trans*- $\text{ReCl}_4(\text{PEt}_3)_2$ is depicted in Figure 4. Information pertinent to the data collection and structure refinement is given in Table X. Positional parameters are listed in Table XI, and bond distances and angles are given in Table XII. This compound crystallizes in the triclinic system with the molecule residing on a center of inversion. The central ReCl_4P_2 group has essentially D_{4h} symmetry as can be seen from the distances and angles.

Discussion

Reactions. In their earlier work, Walton and co-workers^{4,5} used somewhat milder conditions, especially in that CO was simply

**Figure 4.** ORTEP diagram of *trans*- $\text{ReCl}_4(\text{PEt}_3)_2$. Atoms are represented as thermal ellipsoids at the 50% probability level.**Table XI.** Positional Parameters and Their Equivalent Isotropic Thermal Parameters for *trans*- $\text{ReCl}_4(\text{PEt}_3)_2$

atom	<i>x</i>	<i>y</i>	<i>z</i>	B^a , Å ²
Re(1)	0.0000	0.0000	0.0000	2.085 (7)
Cl(1)	0.0842 (3)	-0.2166 (2)	0.1786 (3)	3.58 (4)
Cl(2)	0.2065 (2)	0.1012 (3)	0.1412 (3)	3.69 (4)
P(1)	-0.2141 (2)	0.1695 (2)	0.2241 (2)	2.45 (3)
C(1)	-0.4183 (9)	0.269 (1)	0.118 (1)	3.2 (2)
C(2)	-0.258 (1)	0.055 (1)	0.397 (1)	3.3 (2)
C(3)	-0.150 (1)	0.3298 (9)	0.358 (1)	3.5 (2)
C(4)	-0.551 (1)	0.382 (1)	0.251 (2)	4.9 (2)
C(5)	-0.340 (1)	-0.074 (1)	0.327 (1)	4.1 (2)
C(6)	-0.136 (1)	0.468 (1)	0.252 (1)	4.9 (2)

^aSee footnote to Table II.

Table XII. Bond Distances (Å) and Bond Angles (deg) and Their Esd's for *trans*- $\text{ReCl}_4(\text{PEt}_3)_2$

Re(1)–Cl(1)	2.334 (2)	P(1)–C(3)	1.836 (8)
Re(1)–Cl(2)	2.339 (2)	C(1)–C(4)	1.551 (11)
Re(1)–P(1)	2.518 (1)	C(2)–C(5)	1.530 (13)
P(1)–C(1)	1.838 (7)	C(3)–C(6)	1.547 (14)
P(1)–C(2)	1.830 (9)		
Cl(1)–Re(1)–Cl(2)	89.21 (8)	Re(1)–P(1)–C(3)	113.87 (28)
Cl(1)–Re(1)–Cl(2)'	90.79 (8)	C(1)–P(1)–C(2)	105.91 (39)
Cl(1)–Re(1)–P(1)	91.90 (6)	C(1)–P(1)–C(3)	107.07 (35)
Cl(1)–Re(1)–P(1)'	88.10 (6)	C(2)–P(1)–C(3)	102.16 (39)
Cl(2)–Re(1)–P(1)	91.07 (6)	P(1)–C(1)–C(4)	114.09 (60)
Cl(2)–Re(1)–P(1)'	88.93 (6)	P(1)–C(2)–C(5)	114.56 (60)
Re(1)–P(1)–C(1)	112.52 (25)	P(1)–C(3)–C(6)	114.80 (63)
Re(1)–P(1)–C(2)	114.41 (23)		

(13) Cotton, F. A.; Daniels, L. M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, C39, 1495.

Table XIII. Infrared Spectra and Force Constants

compd	freq, cm ⁻¹		force constants, mdyn/Å			
	obsd	calcd	k ₁	k ₂	k ₃	k ₄
Re(CO) ₅ Cl ^a	2155	2155	15.98	17.52	...	0.25
	2046	2046				
	1983	1983				
<i>cis</i> -Re(CO) ₄ (PEt ₃)Cl	2102	2101	16.44	15.74	14.71	0.24
	1997	1997				
	1987	1986				
	1943	1942				
	2045	2045				
<i>mer</i> -Re(CO) ₃ (PEt ₃) ₂ Cl	1940	1940	14.50	15.98	...	0.39
	1887	1887				
	1912	1912				
	1912	1912				
Re(CO) ₂ (PEt ₃) ₂ Cl ₂	1912	1912	15.56	(0.40)

^a See ref 14.

bubbled through the reaction mixtures at atmospheric pressure. They also used toluene, ethanol, and 2-methoxyethanol as solvents, whereas we have used dichloromethane. We have also used a pressure bomb with CO at about 120 atm. The general course of the reactions does not differ greatly, however, except that we see consequences of the greater pressure of CO in three ways. (1) In the more reducing atmosphere that prevails, we did not find any Re₂Cl₅(PEt₃)₃ or any ReCO(PEt₃)₃Cl₃, although ReCl₄(PEt₃)₂ was isolated. (2) The most CO-rich products found by Walton et al. were the tricarbonyl molecules, Re(CO)₃(PR₃)₂Cl, whereas we have also obtained Re(CO)₄(PEt₃)Cl. (3) In one instance, under the least forcing conditions, Dunbar and Walton⁵ obtained a small amount of the dicarbonyl Re(CO)₂(PMe₂Ph)₃Cl, which they showed to be the *cis*-(CO)₂, *mer*-(PR₃)₃ isomer. Under our CO pressure, it is not surprising that this compound could not be isolated. We naturally confirm Walton's general finding that no "stable carbonyl derivatives in which the Re-Re bond remains intact" are found.

Structural Results. We have already presented the basic facts concerning the structural results. A few comments concerning the significance of these and their relationship to other data are now warranted.

For *all-trans*-Re(CO)₂(PEt₃)₂Cl₂ (**1**) our X-ray work fully confirms the structure proposed on spectroscopic evidence by Walton. His postulation of the trans arrangement of the CO groups was, of course, on safe ground, but the proposed trans arrangements of the other pairs of ligands lacked proof. The Re-Cl bond length, 2.407 (4) Å, in **1** is significantly shorter than those in the Re(I) compounds, where they are in the range 2.49–2.52 Å. This can be attributed to the greater electrostatic attraction between the formally more highly charged rhenium atoms in **1**. On the other hand, the Re-P and Re-C distances 2.470 (4) and 1.980 (17) Å in **1** lie within the ranges 2.43–2.48 and 1.91–2.03 Å, respectively, for such distances in the Re(I) compounds.

The replacement of one Cl ligand in compound **1** by CO gives compound **2**. This simple replacement causes several bond length changes, all of which are understandable. With a drop of one unit in the formal oxidation state of the rhenium, the Re-Cl distance (2.487 (15) Å in Re(CO)₃(PEt)₂Cl) increases significantly, by ca. 0.08 Å. Upon further substitution of phosphine ligands by CO, as in Re(CO)₄Cl(PEt₃), 2.501 (3) Å, and Re(CO)₅Cl, 2.515 (2) Å, the Re-Cl distance changes only slightly. With the decrease in formal positive charge on the metal atom in going from **1** to **2**, the Re-P distance becomes shorter, however, which indicates an increase in metal to phosphorus dπ→pπ bonding. It would also be expected that Re-CO bonds would become shorter for the same reason, but there is a complication because they are not all equivalent. It must also be noted that there are now three strongly π-acidic CO groups competing for an only slightly larger pool (6 vs. 5) of dπ electrons. In view of all these considerations, the fact that the mean of the Re-CO bond lengths in **2**, 1.974 Å, is slightly less than that in **1** is reasonable.

We shall now turn from compound **1** to concentrate on the set of three homologous Re^I compounds, Re(CO)₃(PEt₃)₂Cl, Re(CO)₄(PEt₃)Cl, and Re(CO)₅Cl, the first two of which have been

studied by us, while the last has been dealt with previously.^{13,14} In all three cases, the Re-C bond trans to the Re-Cl bond is the shortest, as would be expected from qualitative back-bonding considerations. In Re(CO)₄(PEt₃)Cl it is also found that, as expected, the Re-C bond trans to the Re-P bond is intermediate in length. In comparisons between different molecules, however, no regularities that are clearly outside of experimental error are found. This is because the estimated standard deviations on the Re-C bond lengths are all in the range 0.01–0.02 Å and the differences to be expected, e.g. for the Re-C bond trans to Re-Cl as the number of phosphines changes, are only of about this magnitude.

trans-ReCl₄(PEt₃)₂ (**4**) has a structure very similar to that previously reported⁶ for its PMe₂Ph analogue, although full details for the latter have not been presented. The Re-P and mean Re-Cl distances are essentially the same in the two compounds, and it appears that both of these types of bonds have nearly invariant bond lengths in all octahedral complexes where the central ion is Re^{IV}. Thus, the Re-Cl distances in K₂ReCl₆¹⁵ and in [Re(C-H₃CN)₄(CO)₂][ReCl₆],¹⁶ 2.37 Å (with unspecified uncertainty) and 2.354 (7) Å, respectively, are only slightly longer than those in compound **4**, 2.337 [3] Å; this is not unexpected in view of the greater Cl-Cl repulsion in the ReCl₆²⁻ ion with its overall negative charge. The Re-P distance of 2.518 (2) Å is essentially the same as that in the [ReCl₅(PEt₃)]⁻ ion.¹⁷

CO Stretching Force Constants. The sets of force constants for compounds **2** and **3** correlate satisfactorily with their structures and show logical relationships among themselves. In each case there is a qualitative relationship between the Re-CO distances and the *k* values, as expected. The greater the Re-C distance, the less back-donation, and the higher the CO bond order. Moreover, in the tetracarbonyl compound, the force constant for a given type of CO (i.e., CO trans to CO, or CO trans to Cl) is greater, by 0.2–0.4 mdyn/Å than for the same type CO in the tricarbonyl. The two systems are isoelectronic, and the metal has the same formal oxidation number; thus this is to be expected. When a comparable pool of dπ electrons has to be spread over a larger number of competing CO groups, each one gets a smaller share.

The CO stretching constants appear to provide a basis for comparing degrees of back-bonding from one molecule to another that was not available (as noted above) on the basis of the Re-C distances. For instance, the force constants for CO groups trans to Cl atoms decrease steadily (15.98, 14.71, 14.50 mdyn/Å) as the number of phosphine substituents increases. Similarly, the force constants for CO groups in the linear OC-Re-CO unit also decrease (17.52, 16.44, 15.98 mdyn/Å) as the number of phosphine ligands increases. In view of these two trends, it is not

(14) Kaesz, H. D.; Bau, R.; Hendrickson, D.; Smith, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 2844.(15) Aminoff, G. Z. *Kristallogr., Kristallphys., Kristallchem.* **1936**, *94A*, 246.(16) Cotton, F. A.; Daniels, L. M.; Schmulbach, C. D. *Inorg. Chim. Acta* **1983**, *75*, 163.

(17) Bucknor, S.; Cotton, F. A.; Reid, A. H., Jr.; Schmulbach, C. D., unpublished observations.

surprising that the weighted averages of the CO force constants for each molecule also decrease (17.21, 15.72, 15.48 mdyn/Å) in the same way.

Concluding Remarks. This work, in conjunction with recent work from the Walton group,^{4,5} clearly demonstrates the synthetic potential for compounds containing multiple bonds between metal atoms when they are treated with reactants such as CO that can sever the M-M bond. In addition, since CO is also a reducing agent, the oxidation state of the metal may also be changed. Thus, as has now been shown, if the time, CO pressure, and temperature are varied, a wide variety of products is available, and the procedure can, in principle, be optimized on the preferred production of one relative to another. We have not, in this work, actually determined precisely the optimum conditions for each possible product (except perhaps for $\text{ReCl}(\text{CO})_5$, where highest CO

pressure, longest reaction time, and higher temperatures are clearly desirable), but the basis has been laid for such optimization, should it be desired.

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Registry No. 1, 66841-01-8; 2, 66841-03-0; 3, 100815-71-2; 4, 24551-06-2; $\text{Re}_2\text{Cl}_6(\text{PEt}_3)_2$, 19584-31-7; $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$, 55400-06-1; $\text{Re}(\text{CO})_4\text{Cl}(\text{PEt}_3)$, 100897-58-3; $\text{Re}(\text{CO})_5\text{Cl}$, 14099-01-5.

Supplementary Material Available: Tables of anisotropic thermal parameters and observed and calculated structure factors (39 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of California, Davis, California 95616

Mononuclear Cobalt(II) Complexes Having Alkoxide and Amide Ligands: Synthesis and X-ray Crystal Structures of $[\text{Co}(\text{Cl})(\text{OC}-t\text{-Bu}_3)_2\cdot\text{Li}(\text{THF})_3]$, $[\text{Li}(\text{THF})_{4.5}][\text{Co}\{\text{N}(\text{SiMe}_3)_2\}(\text{OC}-t\text{-Bu}_3)_2]$, and $[\text{Li}\{\text{Co}\{\text{N}(\text{SiMe}_3)_2\}(\text{OC}-t\text{-Bu}_3)_2\}]$

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The syntheses and first structural characterizations of cobalt(II) alkoxide complexes are described. These are the compounds $[\text{Co}(\text{Cl})(\text{OC}-t\text{-Bu}_3)_2\cdot\text{Li}(\text{THF})_3]$ (1), $[\text{Li}(\text{THF})_{4.5}][\text{Co}\{\text{N}(\text{SiMe}_3)_2\}(\text{OC}-t\text{-Bu}_3)_2]$ (2), and $[\text{Li}\{\text{Co}\{\text{N}(\text{SiMe}_3)_2\}(\text{OC}-t\text{-Bu}_3)_2\}]$ (3). In all of these complexes Co(II) has the rare distorted trigonal-planar geometry. Other features of interest in these structures involve the inclusion of LiCl as a ligand 1, the solvated lithium cation in 2 having pseudo-five-coordination rather than four-coordination, and agostic interactions between ligand CH_3 's and Co or Li in 3. Crystallographic data with Mo K α ($\lambda = 0.71069$ Å) at 140 K: (1) $a = 12.329$ (15) Å, $b = 12.614$ (11) Å, $c = 15.440$ (18) Å, $\alpha = 78.46$ (8)°, $\beta = 68.77$ (8)°, $\gamma = 64.86$ (7)°, $Z = 2$, space group $P\bar{1}$; (2) $a = 11.491$ (3) Å, $b = 16.143$ (6) Å, $c = 31.343$ (9) Å, $\beta = 99.64$ (2)°, $Z = 4$, space group $P2_1/n$; (3) $a = 16.150$ (10) Å, $b = 11.485$ (6) Å, $c = 20.762$ (11) Å, $\beta = 108.90$ (4)°, $Z = 4$, space group Ic . For 1, $R = 0.064$, for 2, $R = 0.080$, and for 3, $R = 0.055$.

Introduction

Over the last few years there has been increasing interest in the synthesis and reactivity of alkoxide and aryloxo complexes of transition metals.¹ For the most part, this work has been confined to early transition elements such as Ti,² Zr,³ Ta,⁴ Cr,⁵ Mo,^{6,7} or W.⁸ Very few reports have dealt with the later elements. The sole exceptions to this generalization involve the work of Wilkinson and co-workers, who have described $-\text{OC}(\text{H})-t\text{-Bu}_2$ ⁹ or 1- and 2-adamantoxy¹⁰ derivatives of Cr, Mn, Fe, and Co.

However, only one structural characterization (of an iron alkoxide) has been published for elements to the right of the manganese triad.⁹ No reports have appeared for either cobalt or nickel derivatives. A number of other structural determinations, however, have dealt with closed-shell Cu(I) complexes.¹¹ In this laboratory, work has concentrated on the use of large alkoxo and amido groups to achieve low coordination numbers among the elements $\text{Cr} \rightarrow \text{Ni}$.^{6,12-15} This work has led to the characterization of interesting species; for example, the first instance of a three-coordinate, d^8 , Ni(II)¹⁵ complex and a distorted T-shaped Cr(II)⁶ geometry. We now describe further extensions involving the $-\text{OC}-t\text{-Bu}_3$ and $-\text{N}(\text{SiMe}_3)_2$ ligands that have allowed the isolation and first¹⁶ structural characterization of novel cobalt(II) complexes involving alkoxide ligands. These are $[\text{Co}(\text{Cl})(\text{OC}-t\text{-Bu}_3)_2\cdot\text{Li}(\text{THF})_3]$ (1),

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