

(CNMe)₆²⁺ excited state more efficiently or that radical escape (*k*₁) occurs less efficiently than in the case of Pd₂(CNMe)₆²⁺. These questions are being explored further in ongoing studies.

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Registry No. [Pd₂(CNMe)₆][PF₆]₂, 56116-48-4; [PdPt(CNMe)₆][PF₆]₂, 60767-38-6; [Pt₂(CNMe)₆][BF₄]₂, 60767-37-5; [PdCl(CNMe)₃][PF₆], 69108-81-2; [PdBr(CNMe)₃][PF₆], 69108-67-4; [PtCl(CNMe)₃][BF₄], 96193-92-9; [PtBr(CNMe)₃][BF₄], 96164-80-6; ·Pt(CNMe)₃⁺, 96164-81-7; ·Pd(CNMe)₃⁺, 96164-82-8; CCl₄, 56-23-5; CBr₄, 558-13-4.

Reactions of Re₂Cl₄(dppm)₂ with Carbon Monoxide That Proceed with Retention of the Metal–Metal Bond: Synthesis of Re₂Cl₄(dppm)₂(CO)_{*n*} (*n* = 1, 2) and the Structural Characterization of Cl₂Re(μ-Cl)(μ-CO)(μ-dppm)₂ReCl(CO)

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Abstract: The triply bonded dirhenium(II) complex Re₂Cl₄(dppm)₂ (dppm = bis(diphenylphosphino)methane) reacts with carbon monoxide to give the carbonyl complexes Re₂Cl₄(dppm)₂(CO)_{*n*} (*n* = 1 or 2). These results provide for the first time evidence as to the nature of the intermediates that are formed in the cleavage of the electron-rich metal–metal triple bond ($\sigma^2\pi^4\delta^2\delta^*2$ configuration) by π -acceptor ligands. The neutral complex, Cl₂Re(μ-Cl)(μ-CO)(μ-dppm)₂ReCl(CO), which has been characterized by X-ray diffraction, crystallizes in the monoclinic system, space group C2/c, with *a* = 22.877 (6) Å, *b* = 11.044 (3) Å, *c* = 22.726 (5) Å, β = 123.02 (2)°, *V* = 4814 (4) Å³, and *Z* = 4. The crystal structure was refined to residuals of *R* = 0.0298, *R*_w = 0.0285, and quality-of-fit = 1.043. The Re–Re bond distance is 2.584 (1) Å, and the molecule comprises a pair of distorted, edge-sharing octahedra. The bridging and terminal Cl and CO ligand sites are disordered in a well-defined manner. A comparison of the spectroscopic properties (IR, and ¹H, ³¹P{¹H} and ¹³C{¹H} NMR) of the dicarbonyl complex with those of its ¹³CO labeled analogue accord with the structure found in the solid state, although ³¹P{¹H} and ¹³C{¹H} NMR spectroscopy show that there is a fluxional process that renders the carbonyl ligands equivalent between room temperature and ca. –20 °C. The monocarbonyl has been shown by IR spectroscopy to exist as a mixture of two isomers both in the solid state and in solution. The NMR spectral properties of this complex (¹H, ³¹P{¹H}, and ¹³C{¹H}) are consistent with an A-frame ↔ non-A-frame fluxionality that keeps the CO ligand bound to a single rhenium atom only.

The reactions of π -acceptor ligands with dimetal complexes that contain metal–metal multiple bonds have been studied extensively.^{2–4} It is well-known, for example, that quadruply bonded Mo₂⁴⁺^{5–7} and Re₂⁶⁺^{8–11} complexes undergo cleavage reactions with isocyanide ligands and with carbon monoxide to afford stable mononuclear species. Similarly, complexes of the type Re₂X₄–

(PR₃)₄ (X = Cl or Br; PR₃ = PEt₃ or P-*n*-Pr₃) possessing a triple bond and a $\sigma^2\pi^4\delta^2\delta^*2$ electronic configuration react with CO to yield the monomeric products ReCl(CO)₃(PR₃)₂ and/or *trans*-ReCl₂(CO)₂(PR₃)₂ that are the results of reductive and nonreductive cleavage, respectively.¹² We have also investigated the carbonylation reactions of the series [Re₂Cl₄(PMe₂Ph)₄]^{*n*+} (*n* = 0, 1, or 2),¹³ in which the Re(I) complexes ReCl(CO)₂(PMe₂Ph)₃ and ReCl(CO)₃(PMe₂Ph)₂, as well as the mononuclear Re(III) carbonyl ReCl₃(CO)(PMe₂Ph)₃, are the principle CO-containing products.¹¹

In none of the aforementioned studies were we able to isolate and identify any reaction intermediate that contained a dinuclear metal–metal bonded unit. However, by resorting to the much more kinetically stable dppm-bridged complex Re₂Cl₄(dppm)₂ (dppm = bis(diphenylphosphino)methane),^{14,15} we have recently succeeded

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in isolating and structurally characterizing the novel A-frame molecule (*t*-BuNC)ClRe(μ -Cl)(μ -dppm) $_2$ ReCl $_2$.^{16,17} With a similar objective in mind, we have turned our attention to the reactions of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ with CO. We now report the successful isolation of the complexes $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_n$ ($n = 1$ or 2), the first examples of dinuclear carbonyl derivatives of this type of complex in which a M-M bond is retained. The X-ray crystal structure of the dicarbonyl complex $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$ was determined, and these results are discussed in conjunction with the data obtained from variable-temperature ^{31}P and ^{13}C NMR spectral studies.

Experimental Section

Starting Materials. The complex $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ was prepared as described previously¹⁵ from the reaction of $\text{Re}_2\text{Cl}_6(\text{P-}i\text{-Bu}_3)_2$ with bis(diphenylphosphino)methane (dppm). Commercial reagents and solvents were used as received and stored over molecular sieves. Bis(diphenylphosphino)methane was obtained from Strem Chemicals and used without further purification. The ^{13}C labeled carbon monoxide was 99% enriched and was purchased from Stohler Isotope Chemicals. Unlabeled carbon monoxide was purchased from Matheson Gas Products and was dried before use.

Reaction Procedures. All reactions were carried out in a dry atmosphere, and the reaction vessels were filled with dinitrogen before introduction of the reactant gas. Solvents were deoxygenated by thoroughly purging with N_2 gas before use.

(A) Reactions of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ with CO. (i) $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$. In a typical reaction, $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ (0.20 g, 0.156 mmol) was dissolved in 10 mL of dry, deoxygenated dichloromethane and placed in a 50-mL three-necked round-bottomed flask fitted with a stopcock, a rubber septum, and a gas inlet tube. A slow stream of carbon monoxide was passed through the purple solution for 5 min at room temperature. The resulting amber solution was treated with 5 mL of diethyl ether and chilled to 0 °C for 1 h. The red-brown crystals were filtered off, washed with diethyl ether, and dried. The filtrate was reduced in volume and additional diethyl ether was added to yield more product; combined yield 0.18 g (88%). Anal. Calcd for $\text{C}_{51}\text{H}_{44}\text{Cl}_4\text{O}_4\text{P}_4\text{Re}_2$: C, 46.72; H, 3.40. Found: C, 47.58; H, 3.99. The ^1H NMR of this sample showed the presence of diethyl ether of crystallization, thereby accounting for the slightly high C and H microanalyses.

This same product was obtained when acetone (20 mL) was used as the reaction solvent. The complex was obtained by addition of diethyl ether or hexane to the filtered reaction solution; yield 0.16 g (78%).

(ii) $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$. A solution that contained $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ (0.50 g, 0.39 mmol) in dichloromethane (15 mL) was treated with CO(g) for 3 h at room temperature. The resulting green solution, which contained some green precipitate, was treated with copious amounts of diethyl ether to produce small green crystals. These were filtered off and dried; yield 0.51 g (97%). Anal. Calcd for $\text{C}_{52}\text{H}_{44}\text{Cl}_4\text{O}_4\text{P}_4\text{Re}_2$: C, 46.64; H, 3.31; Cl, 10.59. Found: C, 45.97; H, 3.84; Cl, 11.07. Alternatively, the reaction mixture can be refluxed for 1.5–2 h to give the same product, but this procedure is less convenient because of the evaporation of much of the solvent resulting from the constant flush of CO(g) through the system. The green crystals have moderate solubility in dichloromethane and chloroform, but they otherwise possess very low solubility in common organic solvents.

An analogous synthetic procedure to the one described above but with acetone or toluene as the reaction solvent gave the same dicarbonyl product in yields of 90% or greater.

(iii) $\text{Re}_2\text{Cl}_4(\text{dppm})_2(^{13}\text{CO})$. An evacuated three-necked 100-mL round-bottomed flask that contained 0.25 g (0.195 mmol) of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ and 15 mL of dichloromethane was connected to a 250-mL flask that was charged with 99% enriched ^{13}CO gas. The contents of the two vessels were then allowed to equilibrate. The purple solution changed to an amber color within 15 min, and the addition of an excess of diethyl ether precipitated a crystalline red-brown product; yield 0.21 g (84%). This material exhibited similar properties to those observed for $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$ except for the expected shifts in the $\nu(\text{CO})$ modes (see Table II).

(iv) $\text{Re}_2\text{Cl}_4(\text{dppm})_2(^{13}\text{CO})_2$. With the use of an experimental setup that was identical with that in section iii, $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ (0.21 g, 0.164 mmol) in 5 mL of dichloromethane was treated with ^{13}CO under static conditions for 12 h. The resulting bright green solution was filtered to yield the appropriate green product, and an additional quantity of complex was obtained upon the addition of methanol to the reaction filtrate;

Table I. Summary of Crystallographic Parameters for $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$

formula	$\text{Re}_2\text{Cl}_4\text{C}_{52}\text{H}_{44}\text{O}_4\text{P}_4$
formula wt	1339.0
space group	$C2/c$
systematic absences	(hkl): $h + k = 2n + 1$ ($h0l$): $l = 2n + 1$
a , Å	22.877 (6)
b , Å	11.044 (3)
c , Å	22.726 (5)
β , deg	123.02 (2)
V , Å 3	4814 (4)
Z	4
d_{calcd} , g/cm 3	1.847
crystal size, mm	$0.1 \times 0.1 \times 0.1$
$\mu(\text{Mo K}\alpha)$, cm $^{-1}$	57.1
data collection instrument	Syntex P1
radiation (monochromated in incident beam)	Mo K α ($\lambda_a = 0.71073$ Å)
orientation reflections, no., range (2θ)	15; $20 < 2\theta < 28^\circ$
scan method	ω - 2θ
data collection range, 2θ , deg.	0–50
no. of unique data, total	2531
with $F_o^2 > 3\sigma(F_o^2)$	2389
no. of observations in refinement	2397 (see text)
no. of parameters refined	297
trans. factors; max, min	calcd 0.56, 0.37; obsd 1.00, 0.72
R^a	0.0298
R_w^b	0.0285
quality-of-fit indicator c	1.043
largest shift/esd, final cycle	0.58
largest peak, e/Å 3	0.74

$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 0.94 / [\sigma^2(|F_o|) + 0.0002F_o^2]$. c Quality of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obsd}} - N_{\text{parameters}})]^{1/2}$.

yield 0.17 g (78%). IR spectral measurements confirmed the identity of this product.

Preparation of Single Crystals of $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$ for Structure Determination. Crystals of $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$ that were suitable for X-ray crystallographic studies were grown by dissolving approximately 0.1 g of this compound in 100 mL of dichloromethane with mild heating. The filtered solution was then reduced in volume to ~60 mL and hexane (50 mL) was added. The solution was allowed to evaporate slowly in air (1 week) to yield a crop of dark green crystals.

(B) X-ray Crystallography. (i) **Data Collection and Reduction.** Geometric and intensity data were taken from a regularly shaped crystal (approximate dimensions $0.1 \times 0.1 \times 0.1$ mm), mounted on a glass fiber, by an automated Syntex P1 diffractometer. The data-collection procedure has been described previously,^{18a} and important parameters are given in Table I. The intensities of three check reflections did not vary significantly through 87 h of X-ray exposure time. Data reduction was carried out by standard methods.^{18b} An empirical absorption correction^{18c} was based on azimuthal scans of several reflections with diffractometer angle χ near 90° .

The crystal was monoclinic, with cell dimensions of $a = 22.877$ (6) Å, $b = 11.044$ (3) Å, $c = 22.726$ (5) Å, and $\beta = 123.02$ (2)°. Systematic absences (Table I) were consistent with either of the two space groups Cc or $C2/c$.

(ii) **Structure Solution and Refinement.** The position of the unique rhenium atom was derived from a Patterson map. All other atoms were located in difference Fourier maps.

The molecule, which lies on a crystallographic center of symmetry (0,0,0 in space group $C2/c$), comprises a pair of distorted octahedra sharing an edge. The coordinated phosphorus atoms are above and below the plane containing the shared edge, and the chlorine and carbonyl ligands are disordered among the six coordination sites lying in that plane. Development of the structure in the acentric space group Cc gave the same disordered, centric pattern, in which each of the coordination sites

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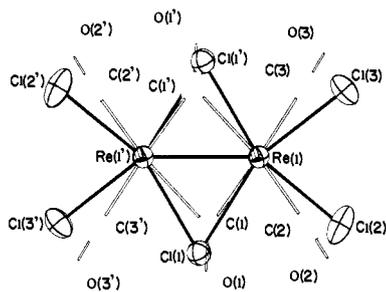
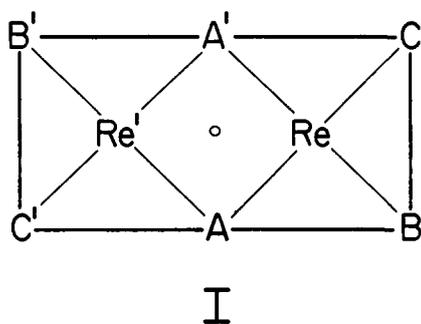


Figure 1. An ORTEP drawing of the equatorial plane in the crystal structure of $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$, showing the positions and labeling of the disordered sites.

in the equatorial plane is "shared" (see below for clarification of what this word means) by a Cl atom and a CO group. We therefore developed and refined the structure with space group $C2/c$, the highest symmetry group accommodating the observed pattern.

In order to explain our refinement strategy, we will now give a brief description of the disordered system. The six crystallographic sites occupied by ligands in the equatorial plane of the molecule are represented schematically in the diagram below. The crystallographic inversion



center relates Re and Re' , A and A' , and so on. From infrared and NMR data we know that the molecule has one bridging CO group and one terminal CO group, which may be either *cis* or *trans* to each other. Let us first suppose that they are *trans* and inquire what site occupancies are to be expected. A little thought will show that the same net result will follow if a *cis* relationship is assumed, and we shall not repeat the analysis in detail for that case. The X-ray crystallography is unable to distinguish between the two stereochemistries. There are four possible orientations of the *trans* molecule, i.e., with CO groups at A and C, at A and B' and then, because of the inversion operation, at A' and C' , and A' and B. The AC and $\text{A}'\text{C}'$ arrangements are equivalent, but they may differ in population from the AB' and $\text{A}'\text{B}$ arrangements. Our development of the structure in space group Cc where the equivalences are not required did not proceed in a way that showed any meaningful difference (which, in any event, is not critical for our purposes). We have been able, however, to distinguish the average occupation of the $\text{A}'\text{B}$ and AB' molecules from that of the AC and $\text{A}'\text{C}'$ molecules, since crystallographic sites B and C are distinct in $C2/c$ as well as in Cc .

With regard to the concept of site "sharing", it must be noted that our designation of sites A, B, and C is schematic. In reality, the Cl sites and carbonyl C and/or O sites are not identical; rather, the disordered C, O, and Cl sites are all between 0.7 and 0.9 Å apart. Figure 1 shows the labeling scheme used for all of the atomic sites in the disordered plane.

The proximity of partially occupied sites in the disordered structure made a fully unrestrained refinement impossible. The model refined was designed to be at once chemically reasonable and completely consistent with the convolution approximation upon which crystallographic least-squares analyses are based.

For the final refinement, the bridging chlorine atom and carbonyl group were each given fixed site-occupancy factors of 0.5. The multiplicities of atoms in the terminal sites were refined in terms of a single variable parameter, in the following way: Carbonyl group $\text{C}(3)\text{-O}(3)$ was assigned a multiplicity x , which was refined freely but was expected to lie in the range 0.0–0.5. The multiplicity of $\text{C}(2)\text{-O}(2)$ was refined as $(\frac{1}{2} - x)$, while those of $\text{Cl}(3)$ and $\text{Cl}(2)$ were $(1 - x)$ and $(\frac{1}{2} + x)$, respectively. Thus, all terminal ligand sites were fully occupied; and the sum of the two crystallographically independent terminal C–O site-occupancy factors was fixed at 0.5, which is equivalent to one terminal CO per molecule.

A common isotropic thermal parameter was refined for atoms C(1) and O(1); in addition, a single isotropic thermal parameter was used for atoms C(2), O(2), C(3), and O(3).

The geometries of all phenyl groups and hydrogen atom positions were idealized before each least-squares cycle. The phenyl groups were refined freely, but all hydrogen atoms in each phenyl group were constrained to ride on a parent carbon atom. A common isotropic thermal parameter was refined for all hydrogen atoms.

Restraints were added to the refinement as observables, but were given low weights. All Re–C and C–O distances, as well as the angles about carbon atoms in the terminal carbonyl groups, were restrained in this way.^{18d}

In all, 297 variable parameters were fitted to 2397 observations; the number of observations includes 8 distance restraints. The final least-squares cycle did not shift any parameter by more than 0.58 times its estimated standard deviation. The refinement gave residuals (defined and summarized in Table I) of $R = 0.0298$, $R_w = 0.0285$, and goodness of fit = 1.043. A difference Fourier map following refinement had maximum and minimum peaks with densities of 0.74 and $-0.50 \text{ e}/\text{\AA}^3$.

The refinement led to site occupancy factors of 0.34 for carbonyl group $\text{C}(3)\text{-O}(3)$ and 0.16 for $\text{C}(2)\text{O}(2)$. Thus, there is not an equal distribution of molecular orientations in the crystal.

Physical Measurements. Infrared spectra were recorded as Nujol mulls between KBr plates or as dichloromethane solutions with an IBM Instruments IR/32 Fourier Transform (4000–400 cm^{-1}) spectrometer. Electronic absorption spectra were recorded on IBM Instruments 9420 UV–visible and Cary 17 spectrophotometers. Electrochemical measurements were carried out by using a Bioanalytical Systems Inc. Model CV-1A instrument on dichloromethane solutions containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values determined as $(E_{p,a} + E_{p,c})/2$ are referenced to SCE at room temperature and are uncorrected for junction potentials. Conductivity measurements were performed with an Industrial Instruments Inc., Model RC-16B2 conductivity bridge. $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Varian XL-200 spectrometer operated at 50.29 and 80.98 MHz, respectively, and with an internal deuterium lock. ^{13}C resonances were referenced to dichloromethane- d_2 ($\delta = 53.8 \text{ ppm}$ vs. Me_4Si) used as the solvent, while for the ^{31}P spectra aqueous 85% H_3PO_4 was used as an external standard. ^1H NMR spectra were obtained on the same instrument at 200.0 MHz, and the residual protons of dichloromethane- d_2 ($\delta = 5.32 \text{ ppm}$ vs. Me_4Si) were used as a reference. Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results and Discussion

(a) Preparation and Preliminary Characterization of $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$ and $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$. The reaction of the parent complex $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ with carbon monoxide proceeds under very mild conditions at atmospheric pressure and room temperature. Reaction in acetone or dichloromethane for short periods (5–10 min) produces the surprisingly stable 1:1 adduct $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$. A color change from purple to amber signals the formation of this species. The red-brown $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$ is usually slightly impure because of its contamination by small amounts of the dicarbonyl species whose formation follows that of the monocarbonyl. Recrystallization from dichloromethane–hexane mixtures produces brick-red crystals which are nonconducting in acetone but which conduct as a 1:1 electrolyte in acetonitrile ($\Lambda_m = 130 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for $c_m = 1 \times 10^{-3} \text{ M}$). This latter observation indicates that $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$ reacts with nitriles, as $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ is known to do.¹⁹ A molecular weight determination shows that this dimetal complex is a monomer in benzene (found 1250, calcd 1311).

The green dicarbonyl species, $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$, can be synthesized from the room-temperature reaction of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ with CO at longer reaction times (1–3 h) in a variety of solvents. Alternatively, it can be obtained by the further reaction of the isolated monocarbonyl species with CO. The yield is essentially quantitative, and the product is analytically pure without recourse to recrystallization. When these reactions are carried out at reflux in solvents such as dichloromethane, acetone, and toluene, the only product is the dicarbonyl complex, even when reaction times as long as 24 h are used. $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$ is sparingly soluble

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Table II. Electrochemical and IR Spectroscopic Data for $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_n$ ($n = 1$ or 2)

	$\nu(\text{CO})_{\text{terminal}}$	$\nu(\text{CO})_{\text{bridging}}$	$E_{1/2}(\text{ox})(2)$	$E_{1/2}(\text{ox})(1)$	$E_{1/2}(\text{red})(1)$	$E_{1/2}(\text{red})(2)$
$\text{Re}_2\text{Cl}_4(\text{dppm})_2(^{12}\text{CO})$	1967 s, 1900 m ^a 1967 s, 1898 m ^b		$\sim +1.8^c$	+0.53	-1.4 ^d	
$\text{Re}_2\text{Cl}_4(\text{dppm})_2(^{13}\text{CO})$	1919 vs, 1854 s ^a					
$\text{Re}_2\text{Cl}_4(\text{dppm})_2(^{12}\text{CO})_2$	1958 vs, 1946 vs ^a 1960 vs ^b	1722 m ^a 1726 m ^b	+1.75	+0.91	-0.57	-1.6 ^d
$\text{Re}_2\text{Cl}_4(\text{dppm})_2(^{13}\text{CO})_2$	1914 vs, 1900 vs ^a	1682 m ^a				

^a Nujol mull. ^b Dichloromethane solution. ^c $E_{\text{p,a}}$. ^d $E_{\text{p,c}}$.

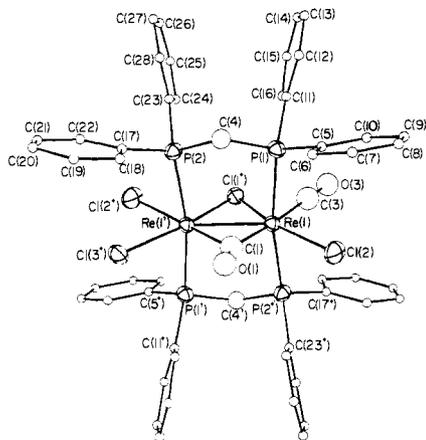


Figure 2. An ORTEP drawing of a single molecule of $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$, showing the atom labeling scheme. Phenyl-group carbon atoms are represented as small circles, for clarity. All other atoms are represented by their 40% probability ellipsoids.

in dichloromethane and chloroform but is otherwise rather insoluble in other common solvents.

Infrared spectral data, along with the cyclic voltammetric electrochemical properties of these complexes and their ^{13}CO labeled analogues (see Experimental Section), are summarized in Table II.²⁰ In the case of the dicarbonyl derivative, bands at ~ 1955 and ~ 1725 cm^{-1} in the IR solution spectrum are assignable to $\nu(\text{CO})$ of terminal and bridging carbonyl ligands, respectively. This assignment has been confirmed by measurements of the IR spectrum of a sample labeled with ^{13}CO , for which the expected shift of these bands to lower energy is observed (Table II). These results accord with the X-ray crystal structure of the dicarbonyl which shows it to be $\text{Cl}(\text{CO})\text{Re}(\mu\text{-CO})(\mu\text{-Cl})(\mu\text{-dppm})_2\text{ReCl}_2$ (vide infra). Note that (as shown later) the splitting of the terminal $\nu(\text{CO})$ mode in the mull spectra of these samples can be attributed to a solid-state effect. A puzzling feature in the IR spectra of $\text{Re}_2\text{Cl}_4(\text{dppm})_2(^{12}\text{CO})$ and $\text{Re}_2\text{Cl}_4(\text{dppm})_2(^{13}\text{CO})$ is the presence of two $\nu(\text{CO})$ bands in both dichloromethane solution and the solid state (Table II). Similar spectroscopic behavior is also observed for carbon tetrachloride, acetone, benzene, and toluene solutions of this complex, although in the two latter solvents the relative intensities of the two $\nu(\text{CO})$ bands are reversed. Recovery of the complex from toluene gave a solid whose Nujol mull spectrum preserved this intensity reversal (i.e., 1970 s and 1898 vs cm^{-1}), but when this material was redissolved in dichloromethane the original spectrum (Table II) returned. We attribute these spectral properties to the presence of two isomers in the solid state and in solution.²¹ These must both contain terminally bound CO and have a low activation energy for interconversion. We believe that this mixture comprises (1) the isomer with axially bound CO, viz., $\text{Cl}_2\text{Re}(\mu\text{-dppm})_2\text{ReCl}_2(\text{CO})$,

(20) The electronic absorption spectra of dichloromethane solutions of the monocarbonyl and dicarbonyl (1500–500 nm) differ quite markedly viz., (λ_{max} in nm) $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO}) \sim 560$ sh, 740 ($\epsilon \sim 100$); $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$ 660 ($\epsilon \sim 100$), 900 sh, 1060 ($\epsilon \sim 300$).

(21) The possibility that the red-brown complex is actually a dicarbonyl species can be discounted since it is formed in essentially quantitative yield upon reacting $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ with 1 equiv of CO. Only very small amounts of unreacted starting material and the dicarbonyl are formed (as monitored by cyclic voltammetry).

Table III. Positional and Isotropic Equivalent Thermal Parameters and Their Estimated Standard Deviations for $\text{Cl}_2\text{Re}(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2\text{ReCl}(\text{CO})^b$

atom	x	y	z	B^a , \AA^2
Re(1)	0.06088 (2)	0.04667 (3)	0.02462 (2)	2.33 (1)
Cl(1)	-0.0492 (3)	0.1544 (4)	-0.0641 (3)	3.03 (9)*
Cl(2)	0.1148 (2)	0.2353 (3)	0.0252 (2)	5.2 (2)
Cl(3)	0.1838 (2)	-0.0023 (4)	0.0949 (2)	4.1 (1)
C(1)	-0.0265 (7)	0.122 (2)	-0.042 (1)	4.6 (3)*
O(1)	-0.0591 (7)	0.209 (1)	-0.0853 (7)	4.6 (3)*
C(2)	0.079 (4)	0.202 (3)	0.003 (3)	5.0 (4)*
O(2)	0.087 (2)	0.288 (2)	-0.023 (2)	5.0 (4)*
C(3)	0.145 (1)	-0.036 (3)	0.087 (1)	5.0 (4)*
O(3)	0.1955 (7)	-0.090 (2)	0.1268 (9)	5.0 (4)*
P(1)	0.0697 (1)	-0.0203 (2)	-0.0746 (1)	2.80 (8)
P(2)	-0.0723 (1)	-0.1304 (2)	-0.1313 (1)	2.84 (8)
C(4)	-0.0184 (4)	-0.0419 (9)	-0.1522 (4)	3.1 (3)
C(5)	0.1078 (5)	0.0935 (9)	-0.1028 (5)	3.5 (4)
C(6)	0.0687 (6)	0.170 (1)	-0.1572 (6)	5.5 (5)
C(7)	0.1013 (7)	0.257 (1)	-0.1759 (7)	6.7 (6)
C(8)	0.1697 (8)	0.267 (1)	-0.1401 (8)	6.7 (7)
C(9)	0.2085 (7)	0.188 (2)	-0.0845 (8)	8.0 (7)
C(10)	0.1780 (6)	0.104 (1)	-0.0675 (6)	6.2 (5)
C(11)	0.1154 (5)	-0.1583 (9)	-0.0698 (5)	3.7 (4)
C(12)	0.1329 (6)	-0.177 (1)	-0.1190 (6)	5.9 (5)
C(13)	0.1657 (7)	-0.284 (1)	-0.1177 (6)	7.3 (6)
C(14)	0.1812 (6)	-0.371 (1)	-0.0688 (6)	6.0 (5)
C(15)	0.1667 (7)	-0.352 (1)	-0.0188 (7)	6.3 (6)
C(16)	0.1345 (5)	-0.2428 (9)	-0.0186 (6)	4.4 (4)
C(17)	-0.1586 (5)	-0.1188 (8)	-0.2098 (4)	3.2 (3)
C(18)	-0.1807 (5)	-0.023 (1)	-0.2556 (5)	4.5 (4)
C(19)	-0.2504 (6)	-0.017 (1)	-0.3152 (6)	5.1 (4)
C(20)	-0.2955 (6)	-0.106 (2)	-0.3277 (7)	7.4 (5)
C(21)	-0.2752 (8)	-0.196 (2)	-0.2816 (8)	9.2 (7)
C(22)	-0.2081 (6)	-0.206 (1)	-0.2256 (6)	6.7 (5)
C(23)	-0.0487 (5)	-0.2882 (8)	-0.1342 (5)	3.9 (4)
C(24)	-0.0196 (6)	-0.364 (1)	-0.0781 (6)	5.0 (5)
C(25)	-0.0051 (8)	-0.4834 (9)	-0.0856 (8)	6.4 (7)
C(26)	-0.018 (1)	-0.525 (1)	-0.1460 (9)	8.4 (9)
C(27)	-0.046 (1)	-0.451 (1)	-0.2021 (8)	11 (1)
C(28)	-0.0586 (9)	-0.330 (1)	-0.1959 (7)	8.8 (8)

^a Atoms with an asterisk were refined isotropically. ^b Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

and (2) the A-frame complex $\text{Cl}_2\text{Re}(\mu\text{-Cl})(\mu\text{-dppm})_2\text{ReCl}(\text{CO})$. Unfortunately, we have not yet been able to grow single crystals of this complex that are suitable for an X-ray structure determination.

Cyclic voltammetric data for the $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_n$ ($n = 0$ or 1) complexes are given in Table II. As reported earlier,¹⁵ $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ exhibits two reversible one-electron oxidations at $E_{1/2} = +0.27$ and $+0.80$ V vs. SCE. In contrast to this, $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$ shows two oxidations, an irreversible process at $E_{\text{p,a}} = +1.8$ V and a reversible couple at $E_{1/2} = +0.53$ V vs. SCE, as well as an irreversible reduction at $E_{\text{p,c}} = -1.4$ V. This shift of the oxidations to more positive potentials relative to $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ and the appearance of a reduction can be attributed to the effect on the metal centers of bonding to a good π -acceptor ligand such as CO.¹¹ This can be envisioned as leading to an increase in the positive charge at the metal center, which causes both an increase in the difficulty of oxidizing such species and an increase in the ease of reduction. A similar argument can be used to explain the appearance of yet another reduction in the

Table IV. Important Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $\text{Cl}_2\text{Re}(\mu\text{-Cl})(\mu\text{-CO})(\mu\text{-dppm})_2\text{ReCl}(\text{CO})^a$

atom 1	atom 2	distance	atom 1	atom 2	distance	atom 1	atom 2	distance
Re(1)	Re(1')	2.584 (1)	Re(1)	C(2)	1.90 (1)	P(1)	C(4)	1.831 (8)
Re(1)	Cl(1)	2.507 (5)	Re(1)	C(3)	1.89 (1)	P(1)	C(5)	1.833 (9)
Re(1)	Cl(1')	2.463 (5)	Re(1)	P(1)	2.483 (2)	P(1)	C(11)	1.817 (10)
Re(1)	Cl(2)	2.418 (3)	Re(1)	P(2')	2.473 (3)	P(2)	C(4)	1.827 (9)
Re(1)	Cl(3)	2.421 (4)	C(1)	O(1)	1.28 (1)	P(2)	C(17)	1.805 (9)
Re(1)	C(1)	1.920 (9)	C(2)	O(2)	1.18 (1)	P(2)	C(23)	1.837 (9)
Re(1)	C(1')	2.14 (2)	C(3)	O(3)	1.17 (1)			

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Re(1')	Re(1)	Cl(1)	57.8 (1)	Cl(1')	Re(1)	P(2')	87.4 (2)	Re(1)	Cl(1)	Re(1')	62.6 (1)
Re(1')	Re(1)	Cl(1')	59.5 (1)	Cl(2)	Re(1)	Cl(3)	77.5 (1)	Re(1)	C(1)	Re(1')	78.7 (7)
Re(1')	Re(1)	Cl(2)	140.58 (9)	Cl(12)	Re(1)	C(1)	86.4 (6)	Re(1)	C(1)	O(1)	148 (2)
Re(1')	Re(1)	Cl(3)	142.0 (1)	Cl(2)	Re(1)	C(3)	96 (1)	Re(1')	C(1)	O(1)	132 (1)
Re(1')	Re(1)	C(1)	54.5 (6)	Cl(2)	Re(1)	P(1)	88.1 (1)	Re(1)	C(2)	O(2)	166 (5)
Re(1')	Re(1)	C(1')	46.8 (4)	Cl(2)	Re(1)	P(2')	83.8 (1)	Re(1)	C(3)	O(3)	177 (3)
Re(1')	Re(1)	C(2)	126 (2)	Cl(3)	Re(1)	C(1')	95.5 (4)	Re(1)	P(1)	C(4)	108.8 (3)
Re(1')	Re(1)	C(3)	123 (1)	Cl(3)	Re(1)	C(2)	92 (3)	Re(1)	P(1)	C(5)	113.8 (3)
Re(1')	Re(1)	P(1)	95.16 (6)	Cl(3)	Re(1)	P(1)	83.8 (1)	Re(1)	P(1)	C(11)	121.6 (3)
Re(1')	Re(1)	P(2')	94.97 (7)	Cl(3)	Re(1)	P(2')	88.4 (1)	C(4)	P(1)	C(5)	103.6 (4)
Cl(1)	Re(1)	Cl(2)	83.2 (1)	C(1)	Re(1)	C(3)	177 (1)	C(4)	P(1)	C(11)	104.1 (4)
Cl(1)	Re(1)	Cl(3)	158.9 (2)	C(1)	Re(1)	P(1)	88.9 (7)	C(5)	P(1)	C(11)	103.2 (4)
Cl(1)	Re(1)	C(1')	104.6 (4)	C(1)	Re(1)	P(2')	96.7 (7)	Re(1')	P(2)	C(4)	109.2 (3)
Cl(1)	Re(1)	C(2)	68 (2)	C(1')	Re(1)	C(2)	173 (2)	Re(1')	P(2)	C(17)	114.6 (4)
Cl(1)	Re(1)	P(1)	87.4 (1)	C(1')	Re(1)	P(1)	97.2 (6)	Re(1')	P(2)	C(23)	120.9 (4)
Cl(1)	Re(1)	P(2')	97.7 (2)	C(1')	Re(1)	P(2')	90.0 (6)	C(4)	P(2)	C(17)	103.6 (4)
Cl(1')	Re(1)	Cl(2)	158.6 (1)	C(2)	Re(1)	P(1)	84 (2)	C(4)	P(2)	C(23)	104.2 (4)
Cl(1')	Re(1)	Cl(3)	82.9 (2)	C(2)	Re(1)	P(2')	90 (2)	C(17)	P(2)	C(23)	102.5 (4)
Cl(1')	Re(1)	C(1)	114.0 (6)	C(3)	Re(1)	P(1)	89 (1)	P(1)	C(4)	P(2)	111.4 (4)
Cl(1')	Re(1)	C(3)	64 (1)	C(3)	Re(1)	P(2')	86 (1)	*Cl(1)	Re(1)	C(3)	176 (1)
Cl(1')	Re(1)	P(1)	98.1 (2)	P(1)	Re(1)	P(2')	169.9 (1)	*Cl(1')	Re(1)	C(2)	174 (2)
								*C(1)	Re(1)	C(2)	72 (3)
								*C(1')	Re(1)	C(3)	76 (1)

^aThe four final angles, marked by an asterisk, are those which would be pertinent to a cis molecule, whereas all others are either for a trans molecule or the same in both cases.

cyclic voltammogram of the dicarbonyl complex. $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$ exhibits two oxidations ($E_{1/2} = +1.75$ and $+0.91$ V) and two reductions ($E_{1/2} = -0.57$ V and $E_{pc} = -1.6$ V vs. SCE). It is obvious from these electrochemical measurements that the coordination of carbonyl ligands to a Re_2^{4+} dinuclear complex profoundly modifies the electronic structure of the metal core.

(b) Crystal Structure of $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$. The positional and isotropic-equivalent thermal parameters for non-hydrogen atoms are given in Table III, and Table IV lists the important bond distances and angles.

The fact that the atoms in the equatorial plane are disordered can be rationalized with reference to Figure 2, which shows the structure and labeling scheme of a single molecule of $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$. The spatial requirements of the molecule are determined predominantly by the dppm ligands, which are related to each other by a center of symmetry, and which occupy the same crystallographic sites in all of the four possible orientations of the molecule described in the Experimental Section. Thus, the crystal packing forces and lattice energy do not discriminate *strongly* among the molecules arranged with CO groups attached through

only one isomer is present in solution, it is likely that only one is present in the crystal. The only evident way to distinguish experimentally which is the correct stereoisomer would be, perhaps, from the magnitude of the ^{13}C - ^{13}C coupling in the fully enriched molecule. Unfortunately this is not possible in practice because the ^{13}C NMR signals are always too broad. At higher temperatures they are broadened by site exchange and at lower temperatures by the nuclear quadrupoles of the rhenium nuclei.

The edge-sharing bioctahedral structure of $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$ is qualitatively similar to that of the doubly bonded (Re_2^{6+} core) complex, $\text{Re}_2\text{Cl}_6(\text{dppm})_2$,¹⁵ although the terminal carbonyl ligand in the present compound is not swept back to the extent that the terminal Cl ligands are in this case or in $\text{Re}_2\text{Cl}_6(\text{dppm})_2$. The average Re-Re-C_{term} angle is 125 [2]°, while the average Re-Re-Cl_{term} is 141.3 [7]° in $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$; the average Re-Re-Cl_{term} angle in $\text{Re}_2\text{Cl}_6(\text{dppm})_2$ was 138.8 [4]°.^{18e}

The present complex, with a formal Re_2^{4+} core, has a Re-Re bond length of 2.584 (1) Å. This is far longer than the bonds observed in triply bonded complexes of the type $\text{Re}_2\text{X}_4\text{L}_4$, which lie within the range of 2.2-2.3 Å.² Thus, the structural results

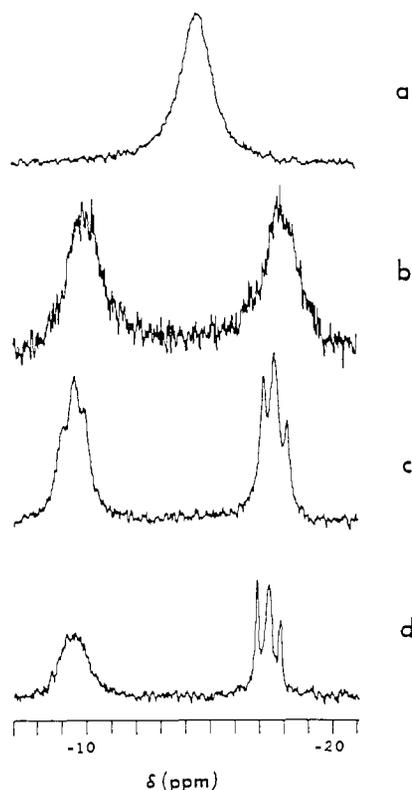


Figure 3. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$ in dichloromethane- d_2 over the temperature range +25 to -35°C : (a) 25°C , (b) -10°C , (c) -20°C , and (d) -35°C .

and $J_{\text{P-H}} = 4.6$ Hz. In the room-temperature (25°C) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of this same complex measured in CD_2Cl_2 , with $\text{Cr}(\text{acac})_3$ (0.02 M) as a relaxation agent, resonances due to the dppm ligand are seen between $\delta = +125$ and $+135$, but at this temperature carbonyl resonances were not detected even when the ^{13}CO -containing complex (99% enrichment) was used. However, when this solution was cooled to -20°C singlets were detected at $\delta = +192$ and $+229$, which may be assigned to a terminal CO ligand and a bridging CO ligand, respectively. Further cooling of the solution to -40°C did not affect the spectrum to any significant extent, but by -55°C both resonances had broadened appreciably, the one at $\delta = +192$ so much so that it had almost disappeared into the base line.

The preceding $^{13}\text{C}\{^1\text{H}\}$ NMR spectral results are best understood in terms of a fluxional process that renders the carbonyl ligands equivalent. The coalescence temperature is around room temperature, but by -20°C the spectral properties are fully in accord with the structure found in the solid state. This interpretation is consistent with the $^{31}\text{P}\{^1\text{H}\}$ spectrum of this complex over the temperature range 25 to -35°C , as shown in Figure 3. A single broad resonance is seen at $\delta = -14.3$ around room temperature, and this collapses and splits into peaks at ca. $\delta \approx -10$ and ca. $\delta \approx -18$ by 0°C . At -20°C an AA'BB' pattern is clearly discernible.²² The coalescence temperature²³ for the $^{31}\text{P}\{^1\text{H}\}$ NMR is ca. 12°C , which suggests a magnitude of about 12.5 kcal/mol for the activation energy, E_a . The mechanism that most likely accounts for this fluxionality is one that involves a "merry-go-round" type of process as has been observed for $\text{Mn}_2(\text{CO})_6(\text{dppm})_2$.²⁴ This involves the Cl and CO ligands in the equatorial plane and will render the phosphorus nuclei equivalent.

The monocarbonyl complex possesses a ^1H NMR spectrum that consists of a complex phenyl region from $\delta = +7.8$ to $+7.0$ and

(22) Over the temperature range -35 to -65°C there is little change in the chemical shifts although the resonances broaden and by -55°C lose their structure.

(23) Since the ^{13}C signals are separated by ca. 1850 Hz while the ^{31}P signals are separated by ca. 650 Hz, it follows that the coalescence temperature for the former will be higher than that for the latter.

(24) Marsella, J. A.; Caulton, K. G. *Organometallics* **1982**, *1*, 274.

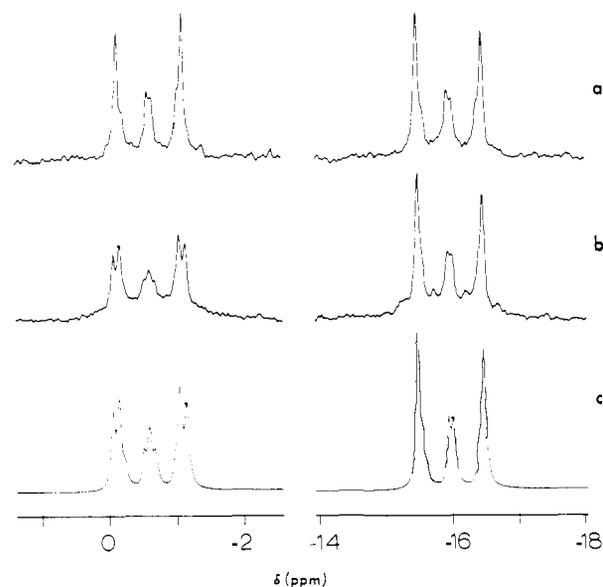


Figure 4. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})$ in dichloromethane- d_2 : (a) $\text{Re}_2\text{Cl}_4(\text{dppm})_2(^{12}\text{CO})$, (b) $\text{Re}_2\text{Cl}_4(\text{dppm})_2(^{13}\text{CO})$, and (c) simulated spectrum of part b.

a methylene pentet at $\delta = +5.61$ ($J_{\text{P-H}} = 4.8$ Hz). This spectrum displays little temperature dependence ($+25$ to -64°C) except for a broadening of the pentet between -44 and -64°C . This pentet pattern for the methylene resonances favors either a non-A-frame type of structure for this complex or the existence of a fluxional process (or processes) that renders the two sides of the molecule equivalent as far as the methylene protons are concerned.^{15,17,19} $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy of the ^{13}CO -labeled complex shows a single carbonyl resonance at $\delta = +199.7$. This is split into a 1:2:1 triplet by coupling with two phosphorus nuclei ($^2J_{^{13}\text{C}-^{31}\text{P}} = 8.1$ Hz). Upon cooling this solution to -50°C , the signal broadens slightly presumably due to coupling with the remaining phosphorus nuclei. $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (at 15°C) reveals two types of phosphorus nuclei in an AA'BB' pattern. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{Re}_2\text{Cl}_4(\text{dppm})_2(^{13}\text{CO})$ shows that the lower field resonance is coupled to the ^{13}CO ligand while the upper field component is unchanged relative to that in the spectrum of $\text{Re}_2\text{Cl}_4(\text{dppm})_2(^{12}\text{CO})$ (Figure 4). Computer simulation of the spectrum, assuming it to be an AA'BB'X spin system, gave excellent agreement with the observed spectrum (Figure 4) with use of the following parameters: $\delta_A = -15.8$, $\delta_B = -0.6$, $J_{\text{AA}'} = 235.6$ Hz, $J_{\text{BB}'} = 229.4$ Hz, $J_{\text{AB}} = 75.5$ Hz, $J_{\text{AB}'} = 3.0$ Hz, and $^2J_{^{31}\text{P},^{13}\text{C}} = 8.1$ Hz.

Taken in conjunction with the IR spectral results (vide supra) we believe that the NMR spectral properties of the monocarbonyl complex (from 25 to -50°C) are consistent with the existence of a fluxional process which interconverts the non-A-frame complex $\text{Cl}_2\text{Re}(\mu\text{-dppm})_2\text{ReCl}_2(\text{CO})$ and the A-frame species $\text{Cl}_2\text{Re}(\mu\text{-Cl})(\mu\text{-dppm})_2\text{ReCl}(\text{CO})$. This should lead to a pentet for the $-\text{CH}_2-$ resonances of the dppm ligands and give $^{31}\text{P}\{^1\text{H}\}$ and $^{13}\text{C}\{^1\text{H}\}$ spectra which reveal coupling of the ^{13}CO ligand to one pair of phosphorus nuclei only. This is exactly what we observe.

(d) A Comparison with Related Systems. The ease with which the dirhenium(II) complexes $\text{Re}_2\text{Cl}_4(\text{PR}_3)_4$ are cleaved by CO to form the compounds $\text{ReCl}_2(\text{CO})_2(\text{PR}_3)_2$, and the reductive cleavage products $\text{ReCl}(\text{CO})_3(\text{PR}_3)_2$,^{11,12} can be contrasted with the tremendously enhanced stability of the dppm-bridged analogue $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ toward CO. This is shown by our isolation of the metal-metal bonded species $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_n$ ($n = 1$ or 2). This provides for the first time evidence as to the nature of the intermediates that are formed in the cleavage of the electron-rich metal-metal triple bond ($\sigma^2\pi^4\delta^2\delta^*$ configuration) by π -acceptor ligands. When taken in conjunction with recent investigations of the reactions between $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ and isocyanide ligands,¹⁷ it is apparent that studies of the reactivity of this dirhenium(II) complex provide a new dimension in the development of the

chemistry of dimetal species that contain metal–metal multiple bonds. The reactions of other complexes of this type, viz., $\text{Re}_2\text{Br}_4(\text{dppm})_2$, $\text{Mo}_2\text{Cl}_4(\text{dppm})_2$, and $\text{W}_2\text{Cl}_4(\text{dppm})_2$, with CO and RNC ligands are currently under investigation.

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Supplementary Material Available: Tables of bond distances and bond angles; anisotropic thermal parameters; hydrogen atom positional parameters; and observed and calculated structure factors for $\text{Re}_2\text{Cl}_4(\text{dppm})_2(\text{CO})_2$ (20 pages). Ordering information is given on any current masthead page.

Homolysis and Electron-Transfer Reactions of Benzylcobalamin

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Abstract: The rate constants have been evaluated for decomposition of the benzylcobalamin species present in acetate buffers ($\text{PhCH}_2[\text{Co}]$) and in dilute perchloric acid ($\text{PhCH}_2[\text{Co}]\cdot\text{H}^+$) in the presence of oxygen, 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (4-HTMPO), and iron(III). Many of these reactions are governed by the initial and rate-limiting homolytic cleavage of the cobalt–carbon bond. In the case of 4-HTMPO, the kinetic inhibition by vitamin B_{12} , ($[\text{Co}^{\text{II}}]$), together with the equilibrium constant for benzyl transfer between benzylcobalamin and penta-aquobenzylchromium(2+), permits the evaluation ($\pm 20\%$) of these rate constants: $[\text{Co}^{\text{II}}]\cdot\text{H}^+ + \text{PhCH}_2\cdot$ ($k = 3.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) and $4\text{-HTMPO} + \text{PhCH}_2\cdot$ ($k = 5.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$). In addition to homolysis, $\text{PhCH}_2[\text{Co}]\cdot\text{H}^+$ reacts with Fe^{3+} by a direct oxidative pathway. The rate varies with $[\text{Fe}^{3+}]$ and $[\text{H}^+]$ consistent with rate-limiting internal electron transfer within a binuclear complex. A three-component mixture of $\text{PhCH}_2[\text{Co}]\cdot\text{H}^+$, O_2 , and ascorbic acid activates O_2 for oxidation of ascorbic acid via binding of O_2 to the base-off form of benzylcobalamin.

Considerable interest has been focused on the reactions of Co–C bonds in organocobalt compounds, especially derivatives of vitamin B_{12} and model complexes. This includes questions of the Co–C bond strength, evaluated from thermodynamic cycles and from kinetic measurements.^{1–6} The latter assignments depend strongly on the differentiation between authentic unimolecular homolysis reactions and various types of bimolecular attack processes. This distinction can be ambiguous, particularly if only oxygen is used as the reagent intended to draw homolysis to completion, since certain chain mechanisms for many O_2 reactions can show a zeroth-order dependence on $[\text{O}_2]$ and yet involve a mechanism with steps other than homolytic cobalt–carbon bond cleavage.⁷ That is one of the issues addressed in this study.

Until recently, certain unknown organocobalamins were thought incapable of isolation owing to steric constraints imposed by the corrin ring. Even benzylcobalamin, where electronic effects should dominate, was unknown. Several compounds, including benzylcobalamin, have recently been prepared.⁸ This requires carefully chosen experimental conditions, especially a sufficiently high $[\text{H}_3\text{O}^+]$ to ensure formation of the base-off complex, a more stable form. They owe their existence to the flexibility of the corrin ring, which adopts a “downward” distorted configuration in response to the steric and electronic demands of the cobalt–alkyl interaction.⁸ This in turn promotes the rupture of the bond between cobalt and the axial base, 5,6-dimethylbenzimidazole. Thus, the secondary alkylcobalamins exist primarily in the “base-off” form, and the less sterically strained benzylcobalamin exists as a pH-dependent mixture of the two.⁹

In part, this work concerns the reaction of benzylcobalamin with oxygen and its relation to unimolecular homolysis. The original report of the oxygen reaction⁹ concluded that it proceeded by unimolecular homolysis but was based upon evidence we consider to be indicative but not definitive. As it so happens, that

assignment has been substantiated by the more detailed results reported here. We have in addition found that benzylcobalamin undergoes oxidative cleavage by reaction with iron(III) ions, that it equilibrates the benzyl group between itself and chromium(II) ions, and that it activates O_2 for oxidation of ascorbic acid.

Results and Interpretation

Homolysis. The decomposition of benzylcobalamin in the presence of oxygen follows first-order kinetics. When conditions chosen were the same as employed previously,⁹ the values agreed well (Table I). The rate constants are independent of $[\text{O}_2]$ (0.3–1.2 mM, air-saturated and oxygen-saturated solution). This was true for both species of benzylcobalamin— $\text{PhCH}_2[\text{Co}]$, the more reactive base-on form existing in buffer solutions (e.g., 0.1 M acetate buffer at pH 5.5 and 1 M phosphate buffer) as well as $\text{PhCH}_2[\text{Co}]\cdot\text{H}^+$, the longer-lived base-off form present at lower pH (e.g., in 1 M H_3PO_4 and in $\text{HClO}_4/\text{LiClO}_4$ solutions).

Three kinetic tests must be satisfied for the observed rate of aerobic decomposition really to correspond to the rate of homolysis. The first-order rate constant must be independent of the concentration of radical scavenger, it must be the same when different scavengers are used, and it must decrease with addition of one homolysis fragment (in this case, $[\text{Co}^{\text{II}}]$), as the radical–cobalt

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