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Synthesis and Characterization of (η^3-CPh$_3$)Re(CO)$_4$, a Thermal Precursor for Generation of the Re(CO)$_5$ Radical

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Reaction of NaRe(CO)$_5$ with Ph$_3$CPF$_6$ affords Re(CO)$_4$(η^3-CPh$_3$) (**1**). Complex **1** reacts readily with CO at room temperature to give the $^\bullet$Re(CO)$_5$ radical, which forms Re$_2$(CO)$_{10}$ in the absence of trapping agents. The radical reacts with CCl$_4$ to give Re(CO)$_5$Cl and with Fe(CO)$_5$ to give Re$_2$Fe(CO)$_{14}$ (**2**). Compounds **1** and **2** have been structurally characterized. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with lattice parameters a = 11.062 (2) Å, b = 11.383 (1) Å, c = 17.961 (3) Å, α = 104.62 (1)°, β = 94.77 (2)°, and γ = 98.52 (1)°. The final R value was 3.7%. The structure shows a Re(CO)$_4$ moiety coordinated to the central carbon of the triphenylmethyl unit and two carbons of one phenyl ring. Complex **2** crystallizes in the monoclinic space group $C2/m$ with lattice parameters a = 12.083 (3) Å, b = 14.705 (4) Å, c = 11.822 (3) Å, and β = 97.43 (2)°. The final R value was 3.4%. The structure shows a linear Re–Fe–Re array.

Introduction

There has been considerable recent interest in the chemistry of 17-electron metal-centered radicals.[1] These very labile species are postulated as intermediates in both thermal[2] and photochemical[3] reactions of metal–metal bonded dimers. In the case of $^\bullet$Re(CO)$_5$, recent results have clearly established that thermal homolysis of Re$_2$(CO)$_{10}$ does not occur readily.[4] The method of choice for generation of $^\bullet$Re(CO)$_5$ and indeed most transition-metal-centered radicals is photolysis of a metal–metal bond. Such studies are often complicated by competing photochemical ligand labilization from the starting materials.[5]

In the hope of securing a thermal source of metal-centered radicals, we have pursued the possibility of thermal homolyis of weak metal–carbon σ bonds. Promising candidates for this role would appear to be metal triphenylmethyl complexes, M–CPh$_3$. A search of the literature revealed only one reported example of such a compound. The reaction of NaRe(CO)$_5$ with Ph$_3$CCl was reported to afford (CO)$_5$Re–CPh$_3$.[6] We have reinvestigated this reaction and find that the product is correctly formulated as (CO)$_4$Re(η^3-CPh$_3$) (**1**). Complex **1** has indeed proven to be a thermal source of rhenium(0) radical species. We report here our results on the generation of the Re(CO)$_5$ radical from **1** by addition of carbon monoxide under mild thermal conditions.

Experimental Section

All reactions except those involving addition of carbon monoxide were performed under a nitrogen atmosphere with standard Schlenk techniques. Carbon monoxide (research grade, Matheson) was used without further purification. The solvents tetrahydrofuran and heptane were distilled from K/benzophenone prior to use. Deuteriated tetrahydrofuran was dried over Na/K/benzophenone and stored under vacuum. (Ph$_3$C)PF$_6$ was synthesized by using a previously reported procedure for (Ph$_3$C)BF$_4$ and substituting HPF$_6$ for HBF$_4$.[7] All other reagents were obtained from commercial sources and used without further purification unless otherwise noted. IR spectra were recorded on a Perkin-Elmer 337 Grating infrared spectrometer or a Nicolet 5-SX FT-IR instrument. NMR spectra were obtained at 250 or 500 MHz on a Bruker WM250 or WM500 spectrometer. Mass spectral data were obtained with a Hewlett Packard 5985 GC-MS instrument. Elemental analyses were performed by Galbraith Analytical Laboratory. The X-ray structural characterization of **2** was done by the Crystalytics Co.

Preparation of (η^3-CPh$_3$)Re(CO)$_4$ (1). Re$_2$(CO)$_{10}$ (750 mg, 1.15 mmol) was dissolved in 150 mL of THF, and the solution was stirred over sodium amalgam (380 mg of Na, 16.5 mmol; 38 g of Hg) for 1 h. After the suspension was allowed to settle for 1 h, the dark orange solution was filtered and cooled to −78 °C, and Ph$_3$CPF$_6$ (880 mg, 2.26 mmol) was added. The solution turned dark red immediately and gradually lightened to orange as it warmed to room temperature over a 1.5-h period. THF was removed under vacuum, and the resulting brownish yellow residue was extracted with heptane (3 × 50 mL). The heptane extracts were filtered, concentrated, and eluted through a 1-in. column of silica gel. The resulting yellow solution was concentrated and cooled to −20 °C to give 466 mg of **1** (0.86 mmol, 37.4% based on Re$_2$(CO)$_{10}$) as bright yellow crystals: mp 110 °C dec; IR (heptane) ν(CO) 2089 (w), 1995 (s), 1984 (m), 1949 (m) cm^{-1}; IR (THF) ν(CO) 2087 (w), 1994 (s), 1978 (m), 1939 (m) cm^{-1}; ^{1}H NMR (THF-d_8, 273 K, 500 MHz) δ 7.46 (t, J = 8 Hz, 2 H, coordinated meta), 7.27 (s, broad, 4 H, free ortho), 7.21 (t, J = 8 Hz, 4 H, free meta), 7.15 (t, J = 8 Hz, 1 H, coordinated para), 7.06 (t, J = 8 Hz, 2 H, free para), 6.64 (d, J = 8 Hz, 2 H, coordinated ortho); ^{13}C{^{1}H} NMR (THF-d_8, 173 K, 250 MHz) δ 193.4 (1 C, CO), 188.8 (1 C, CO), 187.8 (2 C, CO), 150.6 (2 C, free ipso), 135.5 (2 C, coordinated ortho), 132.6 (4 C, free meta), 129.4 (4 C, free ortho), 126.5 (2 C, free para), 124.9 (1 C, coordinated para), 118.5 (1 C, coordinated ipso), 102.7 (2 C, coordinated meta); MS m/z 542 (M$^+$), 514 (M$^+$ − CO), 486 (M$^+$ − 2CO), 456 (M$^+$ − 3CO), 428 (M$^+$ − 4CO). Anal. Calcd for C$_{23}$H$_{15}$O$_4$Re. C, 51.02; H, 2.77. Found: C, 51.29; H, 2.87.

Reaction of (η^3-CPh$_3$)Re(CO)$_4$ (1) with CO. A solution of **1** (12.7 mg, 0.023 mmol) in heptane (3 mL) was degassed in a tube equipped with a high-vacuum Teflon stopcock and stirred under a positive pressure of CO (20 psi) for 3 days; during this time a white precipitate formed and the yellow solution lightened in color. An IR spectrum of the supernatant taken after 3 days confirmed that **1** had been entirely consumed and that Re$_2$(CO)$_{10}$ (IR (heptane) ν(CO) 2060 (w), 2010 (s), 1975 (m) cm^{-1}) had been formed.

Attempted Reaction of (η^3-CPh$_3$)Re(CO)$_4$ (1) with Mn$_2$(CO)$_{10}$ in the Presence of CO. Freshly sublimed Mn$_2$(CO)$_{10}$ (15 mg, 0.045 mmol) and **1** (52 mg, 0.09 mmol) were dissolved in heptane (20 mL). The solution was degassed and stirred under CO (20 psi). The only product detectable by IR spectroscopy, formed over an 18-h period, was Re$_2$(CO)$_{10}$.

Reaction of (η^3-CPh$_3$)Re(CO)$_4$ (1) with CCl$_4$ in the Presence of CO. CCl$_4$ (2.04 mg, 0.013 mmol) was added to a heptane solution (7 mL) of **1** (7.2 mg, 0.013 mmol) in a tube equipped with a high-vacuum Teflon stopcock. The solution was degassed and stirred under CO (20 psi). A white precipitate quickly formed that was identified as Re(CO)$_5$Cl by IR spectroscopy (CCl$_4$): ν(CO) 2045, 1980 cm^{-1}; lit.[8] ν(CO) 2046 (s), 1983 (m) cm^{-1}. In the course of 30 min, all starting material had been converted to Re(CO)$_5$Cl.

Reaction of (η^3-CPh$_3$)Re(CO)$_4$ (1) with Fe(CO)$_5$ in the Presence of CO. Formation of Re$_2$Fe(CO)$_{14}$ (2). Fe(CO)$_5$ (72 mg, 0.36 mmol) was added to a heptane solution (20 mL) of **1** (100 mg, 0.18 mmol) in a tube equipped with a high-vacuum Teflon stopcock. The solution was degassed and left under CO (20 psi) for 4 h without stirring; during this time orange needles formed (48 mg, 66% yield based on **1**). The su-

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Table I. Data Collection and Processing Parameters of Compounds **1** and **2**

	1	**2**
mol formula	$C_{23}H_{15}O_4Re$	$C_{14}O_{14}FeRe_2$
fw	541.58	820.4
T, °C	25	25
space group	$P1$	$C2/m$
a, Å	11.062 (2)	12.083 (3)
b, Å	11.383 (1)	14.705 (4)
c, Å	17.961 (3)	11.822 (3)
α, deg	104.62 (1)	90.00
β, deg	94.77 (2)	97.43 (2)
γ, deg	98.52 (1)	90.00
V, Å^3	2147 (1)	2083.0 (9)
no. of formula units per cell (Z)	4	4
density (ρ), g cm^{-3}	1.68	2.616
abs coeff (μ), cm^{-1}	57.58	125
λ(Mo Kα), Å	0.71073	0.71073
R^a	0.037	0.034
$R_w{}^b$	0.046	0.035

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b [\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where N_o = number of observations and N_v = number of variables.

pernatant, containing excess $Fe(CO)_5$ and the organic product, was removed via cannula. The precipitate was dried under vacuum. A sample of the crystals redissolved in hexane showed the presence of a carbonyl-containing species: IR (hexane) ν(CO) 2094 (w), 2021 (s), 1982 (m) cm^{-1}. The organic product formed during the reaction was identified as the triphenylmethyl dimer by comparison of its ^{1}H NMR spectrum to that of an authentic sample.[9] MS: m/z 820 (M^+), 652 ($M^+ - Fe(CO)_4$), 624 ($M^+ - Fe(CO)_5$), 596 ($M^+ - Fe(CO)_6$). Anal. Calcd for $C_{14}O_{14}FeRe_2$: C, 20.49; H, 0.0. Found: C, 20.83; H, 0.29.

X-ray Crystallography. A summary of the procedures used for solving and refining structures for **1** and **2** is given in Table I. Crystals of complex **1** were obtained by slow cooling of an ethyl acetate solution. A crystal of dimensions 0.25 × 0.20 × 0.13 mm was employed. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo Kα radiation. Examination of 25 randomly selected reflections revealed a triclinic unit cell with the following lattice parameters: a = 11.062 (2) Å, b = 11.383 (1) Å, c = 17.961 (3) Å, α = 104.62 (1)°, β = 94.77 (2)°, γ = 98.52 (1)°. The space group was assigned as $P1$ (No. 2), Z = 4, with two molecules of composition $C_{23}H_{15}O_4Re$ forming the asymmetric unit.[10] The calculated density was 1.68 g/cm^3. Of 7575 reflections collected ($2\theta \geq 50°$), 3837 (51%) with $I \geq 3\sigma$ were adjudged observed. The structure was solved by locating the rhenium atom with use of the Patterson synthesis. Iterations of the WFOUR synthesis in DIRDIF resulted in the solution of the entire non-hydrogen structure. The full-matrix refinement of the non-hydrogen atoms resulted in convergence to an unweighted residual of 0.037 and a weighted residual of 0.046. A three-atom fragment of disordered ethyl acetate, the solvent of crystallization, was located in a difference Fourier map. All intramolecular bond distances and angles are within normal ranges.

Crystals of complex **2** were obtained by slow cooling of a heptane solution. The crystal examined was a rectangular parallelpiped of dimensions 0.10 × 0.20 × 0.68 mm. A Nicolet four-circle diffractometer was employed. Examination of 15 reflections revealed a monoclinic unit cell with lattice parameters a = 12.083 (3) Å, b = 14.705 (4) Å, c = 11.822 (3) Å, $\alpha = \gamma$ = 90°, and β = 97.43 (2)°. The space group was assigned as $C2/m$ (No. 12), Z = 4.[10] The calculated density was 2.616 g/cm^3. A total of 2494 independent reflections were collected, of which 1836 had $I \geq 3\sigma$. The structure was solved by using the Patterson method to locate the heavy atoms, followed by full-matrix refinement of all atoms. In the final cycles of cascade block-diagonal refinement, all atoms were refined anisotropically to give a standard unweighted residual of 0.034 and a weighted residual of 0.035.

Results and Discussion

Preparation and Characterization of $Re(CO)_4(\eta^3$-$CPh_3)$ (1). Reaction of $NaRe(CO)_5$ with Ph_3CCl is reported to give a yellow compound formulated as $Re(CO)_5(CPh_3)$.[6] In our hands, this reaction affords very low yields of a tetracarbonyl derivative $Re(CO)_4(\eta^3$-$CPh_3)$ (**1**). Improved yields of **1** (30–40%) were obtained by reaction of $NaRe(CO)_5$ with Ph_3CPF_6 at −78 °C. Compound **1** has been fully characterized by ^{1}H and ^{13}C NMR spectroscopy, infrared spectroscopy, mass spectroscopy, crystal structure determination, and elemental analysis. The infrared spectrum of **1** in the CO stretching region shows a characteristic pattern of four bands, very similar to that of related complexes such as (η^3-C_3H_5)$Re(CO)_4$.[11]

Scheme I

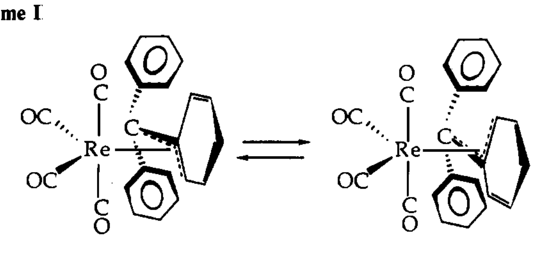

Table II. Selected Bond Lengths and Angles for **1**

(a) Bond Lengths (Å)

Re1–C7	2.29 (1)	C1–C7	1.48 (2)
Re1–C1	2.37 (1)	C1–C2	1.44 (2)
Re1–C2	2.45 (1)	C7–C8	1.56 (2)
Re1–C22	1.94 (2)	C7–C14	1.51 (2)
C21–O2	1.14 (1)	C2–C3	1.45 (2)

(b) Bond Angles (deg)

C20–Re1–C23	174.6 (5)	C22–Re1–C1	126.9 (5)
C22–Re1–C20	89.0 (7)	C23–Re1–C1	82.2 (5)
O2–C21–Re1	180 (2)	C7–C1–C2	119 (1)
C20–Re1–C7	90.9 (5)	C1–C7–C8	114.1 (9)
C21–Re1–C7	101.8 (5)	C1–C7–C14	118 (1)
C22–Re1–C7	163.1 (5)	C8–C7–C14	10 (1)
C23–Re1–C7	93.4 (5)	C1–Re1–C7	37.0 (4)
C20–Re1–C2	83.1 (5)	C1–Re1–C2	34.6 (4)
C21–Re1–C2	162.0 (5)	C1–C2–Re1	69.6 (6)
C22–Re1–C2	99.2 (5)	C1–C7–Re1	74.6 (6)
C23–Re1–C2	101.7 (5)	C8–C7–Re1	123.0 (8)
C20–Re1–C1	103.2 (5)	C14–C7–Re1	113.5 (7)
C21–Re1–C1	136.6 (5)		

The structure of **1** is supported by NMR observations. The ^{1}H NMR spectrum consists of a complex set of resonances in the aromatic region (6.9–7.4 ppm) and a doublet (J = 8Hz) at 6.55 ppm. Decoupling experiments establish that the doublet is due to the ortho protons of a coordinated phenyl ring and allow the assignment of resonances corresponding to the meta and para resonances of the coordinated ring. The remaining aromatic resonances are due to the two noncoordinated phenyl rings. Qualitatively similar spectral data have been reported for η^3-CPh_3 complexes of platinum and palladium.[12] The ^{13}C NMR spectrum of **1** supports the conclusions reached on the basis of ^{1}H NMR data and also exhibits three resonances due to metal carbonyls at 193.6, 188.9, and 187.5 ppm (1:1:2 intensity ratio). These observations imply that **1** undergoes a fluxional process that renders equivalent the two sides of the coordinated phenyl ring as well as the two axial carbonyls (see Scheme I). No additional carbonyl resonances were observed in ^{13}C NMR spectra recorded at lower temperatures (208–273 K, 62.98 MHz), indicating that the dynamic process averaging the axial carbonyls is still rapid at the lowest temperatures reached. In related η^3-benzyl complexes, observation of similar fluxional processes has been attributed to rapid η^3–η^1 interconversion processes.[13] For complex **1**, we were able to observe such a process in a qualitative spin-saturation-transfer experiment. Saturation (298 K) of the resonance due to the ortho protons of the coordinated phenyl ring caused the resonance due to the ortho protons of the noncoordinated rings to decrease in intensity, indicating that formation

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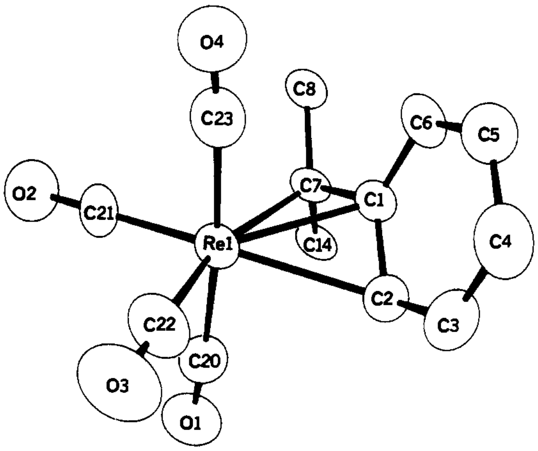
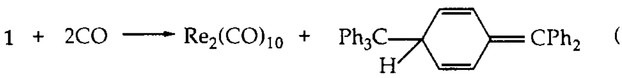


Figure 1. ORTEP projection and labelling scheme for **1**. Non-hydrogen atoms are depicted as 50% probability ellipsoids. Noncoordinated phenyl rings are omitted for clarity.

of a 16-electron σ-bonded isomer of **1** does occur but that this process is much slower than the rapid process that exchanges the two sides of the coordinated ring.

The coordination mode of the triphenylmethyl group has been confirmed by X-ray diffraction (Figure 1). The Re atom shows bonding interactions with the central carbon of the triphenylmethyl unit (Re(1)–C(7) = 2.29 Å), as well as one ortho and the ipso carbon on one phenyl ring (Re(1)–C(1) = 2.37 Å; Re(1)–C(2) = 2.45 Å).

Reactions of (η^3-CPh$_3$)Re(CO)$_4$ (1). Treatment of **1** with CO (20 psi) at room temperature leads to formation of Re$_2$(CO)$_{10}$ and the dimer of the triphenylmethyl radical (eq 1). The organic



(1)

product of the reaction was identified by comparison of its ^{1}H NMR spectrum to that of an authentic sample prepared by reduction of Ph$_3$CCl with zinc.[9]

This reaction presumably proceeds via the intermediacy of Re(CO)$_5$(CPh$_3$), although no direct evidence has been obtained for this species. A consideration of known bond strengths in related compounds leads to the conclusion that this compound probably has a very weak Re–C σ bond. The metal–carbon bond dissociation energy, D[CH$_3$–Re(CO)$_5$], in CH$_3$–Re(CO)$_5$ is 53.2 ± 2.5 kcal/mol[14] while D[CH$_3$–CH$_3$] is 88 kcal/mol.[15] Since the dissociation energy for the central bond in the triphenylmethyl dimer is 11 kcal/mol,[16] the triphenylmethyl radical is stabilized relative to the methyl radical by 38 kcal/mol. Thus, the Re–C σ bond in Re(CO)$_5$(CPh$_3$) probably has a dissociation energy of about 15 kcal/mol.[17] Failure to observe this species is consistent with these considerations.

When the reaction of **1** with CO was carried out in the presence of CCl$_4$, the only organometallic product formed was Re(CO)$_5$Cl. This result is consistent with reported results of trapping photochemically generated $^\bullet$Re(CO)$_5$ with CCl$_4$.[18]

The above evidence indicates that carbonylation of **1** does indeed provide a clean source of $^\bullet$Re(CO)$_5$. We next sought to investigate the reactivity of this radical toward other organometallic species. Carbonylation of **1** in the presence of Fe(CO)$_5$ gave good yields of Re$_2$Fe(CO)$_{14}$ (**2**). It has been shown that Fe(CO)$_5$ does not react with CCl$_4$ under thermal conditions.[19] Thus, it seems likely that formation of **2** involves attack of $^\bullet$Re(CO)$_5$ on an intact Fe(CO)$_5$ molecule. Compound **2** has been previously reported as a low-yield product formed in the photolysis of a mixture of Re$_2$(CO)$_{10}$ and Fe(CO)$_5$.[20] Some difficulty arose in confirming the identity of **2** since our IR spectrum did not completely match the spectrum previously reported.[21] The IR spectrum of a hexane solution of **2** prepared in our laboratory consists of only three bands in the carbonyl stretching region (ν(CO) 2094 (w), 2021 (s), 1982 (s), 1982 (m) cm^{-1}). For idealized D_{4h} molecular symmetry, four IR-active modes are expected (2 A$_{2u}$ + 2 E$_u$). We tentatively attribute the observation of only three bands to overlap of the two E modes, leading to the strong absorption at 2021 cm^{-1}. The previous report of six IR bands[21] for **2** may have been due to some impurities in the sample. Although ancillary data (mass spectrum and elemental analysis) confirmed our formulation of **2**, a single-crystal X-ray diffraction study was undertaken in order to conclusively identify this species. The crystal structure shows a linear Re–Fe–Re array with Re–Fe bond distances of 2.855 (1) Å (Figure 2). Each metal has an octahedral coordination sphere with the carbonyl groups on the Fe atom staggered with respect to the equatorial carbonyls on each Re atom.

Table III. Bond Lengths and Selected Angles for **2**

(a) Bond Lengths (Å)			
Re1–Fe1	2.855 (1)	O11–C11	1.10 (2)
Re1–C11	1.93 (1)	O12–C12	1.15 (2)
Re1–C12	2.00 (1)	O13–C13	1.13 (1)
Re1–C13	2.01 (1)	O14–C14	1.21 (2)
Fe1–C14	1.75 (1)	O15–C15	1.17 (2)
Fe1–C15	1.78 (1)		
(b) Bond Angles (deg)			
Re1–Fe1–Re1′	180.0 (–)	C12–Re1–C13	91.3 (3)
Fe1–Re1–C11	180.0 (–)	C14–Fe1–C15	89.9 (6
Fe1–Re1–C13	88.7 (3)	Re1–C12–O12	179.6 (6)
Re1–Fe1–C14	90.0 (–)	Fe1–C15–O15	179.6 (11)

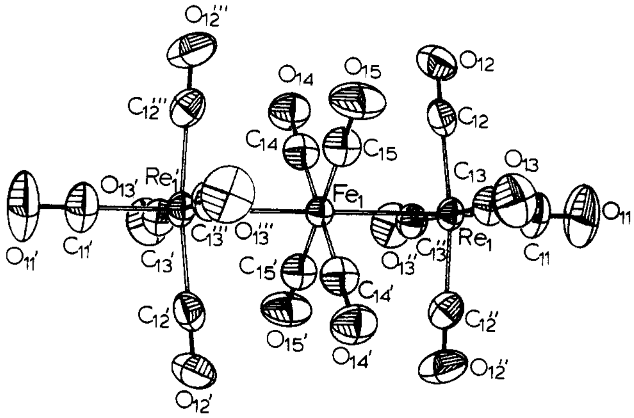


Figure 2. ORTEP projection and labelling scheme for **2**. Atoms are depicted as 50% probability ellipsoids.

The formation of **2** demonstrates the ability of $^\bullet$Re(CO)$_5$ to react with other metal centers, which are themselves thermally inert to radical formation, to form new metal–metal-bonded species. In contrast, when carbonylation of **1** was carried out in the presence of Mn$_2$(CO)$_{10}$, no ReMn(CO)$_{10}$ was formed.[22] Thus, it appears that $^\bullet$Re(CO)$_5$ will react with five-coordinate metal centers such as Fe(CO)$_5$ but does not attack species that are six-coordinate. We are currently investigating reaction of thermally generated $^\bullet$Re(CO)$_5$ with other five-coordinate complexes.

Conclusions

We have shown that **1** reacts with carbon monoxide under mild thermal conditions to give $^\bullet$Re(CO)$_5$. The radical reacts with

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$Fe(CO)_5$ to give the trimetallic species **2**; it is hoped that $^{\bullet}Re(CO)_5$ generated in this fashion will react with other coordinatively unsaturated metal centers to form new metal–metal bonds. We are also investigating the reactivity of **1** toward a variety of two-electron ligands as a preparative route to other Re(0) radicals.

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Supplementary Material Available: For **1** and **2** summaries of the complete X-ray analyses, including tables of positional parameters, distances, angles, and thermal parameters, and for **2** perspective drawings of its two crystallographically independent molecules (34 pages); listings of F_o and F_c for **1** and **2** (34 pages). Ordering information is given on any current masthead page.

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Reactivity of Tetraphosphorus Trichalcogenides with Rhodium(I)- and Iridium(I)–Triphosphane Fragments. Synthesis and Characterization of Mixed-Metal and Unsubstituted-Main-Group-Element Cluster Compounds. Crystal and Molecular Structures of $[(triphos)M(P_3X_3)]\cdot C_6H_6$ (M = Rh, X = S, Se; M = Ir, X = S)

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The reaction of tetraphosphorus trisulfide or tetraphosphorus triselenide with $[MCl(cod)]_2$ (M = Rh, Ir; cod = cycloocta-1,5-diene) in the presence of triphos [triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane, $CH_3C(CH_2PPh_2)_3$] yields the compounds $[(triphos)M(P_3X_3)]\cdot C_6H_6$ [M = Rh, X = S (**1**), Se (**2**); M = Ir, X = S (**3**), Se (**4**)]. The crystal structures of **1**–**3** have been elucidated through complete X-ray analyses. The compounds crystallize in the orthorhombic $P2_1nb$ space group with $Z = 4$ and the following unit-cell dimensions: **1**, $a = 19.109$ (5) Å, $b = 19.445$ (5) Å, $c = 12.319$ (4) Å; **2**, $a = 19.277$ (7) Å, $b = 19.608$ (9) Å, $c = 12.398$ (6) Å; **3**, $a = 19.131$ (9) Å, $b = 19.451$ (9) Å, $c = 12.293$ (6) Å. The compounds contain the (triphos)M system replacing a basal P atom of the cage molecule. ^{31}P NMR data for the compounds, which form systems having six (**3**, **4**) and seven (**1**, **2**) magnetically active nuclei, are reported.

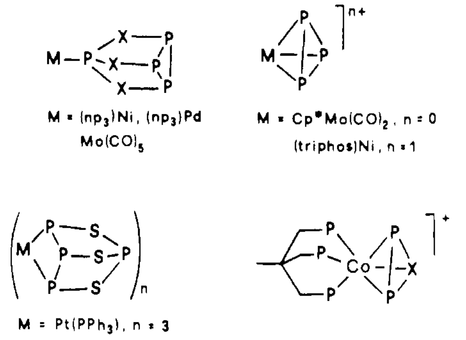
Introduction

Some effort has been recently devoted to elucidating the reactivity of main-group clusters toward transition-metal fragments.[1–6] Among the numerous neutral and ionic species containing unsubstituted main-group elements, the chalcogenides of group V elements, E_4X_3 (E = P, As; X = S, Se), are receiving considerable attention because different types of atoms are present in the cage molecules of these compounds and atoms of the same chemical type have different environments (e.g. apical vs basal pnicogens).

In particular, the intact P_4X_3 (X = S, Se) molecules have been found to coordinate to a metal fragment through the apical P atom in the four-coordinate complexes $[(np_3)M(P_4X_3)]$ [np_3 = tris(2-diphenylphosphinoethyl)amine; M = Ni, Pd; X = S,[7] Se[8]] and in the hexacoordinate complex $[Mo(P_4S_3)(CO)_5]$[9] (Chart I). P_4S_3 reacts with $[IrCl(CO)(PPh_3)_2]$ and $[Pt(C_2H_4)(PPh_3)_2]$ to give di-[10] and trimetallic[11] compounds through the insertion of a metal–ligand fragment into a P–P bond of the cage. Substantial cleavage of the cage molecules, on the other hand, occurs in the reactions with $[Cp^*Mo(CO)_2]_2$ (Cp^* = pentamethylcyclopentadienyl) and with cobalt(II) and nickel(II) tetrafluoroborates in the presence of triphos [triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane]. The molybdenum[12,13] and nickel[14] derivatives contain the cyclo-P_3 unit η^3-bound to the metal fragment, whereas the cobalt compounds[15] incorporate the heterocyclic P_2X units (X = S, Se) η^3-bound to the cobalt moiety. These processes have recently been summarized.[16]

We have investigated the reactions of P_4X_3 (X = S, Se) with the $(triphos)M^I$ (M = Rh, Ir) moieties, which provide the same geometrical environment as the $(triphos)M^{II}$ (M = Co, Ni) fragments, but with the metal in a lower oxidation state. Such reactions yielded the compounds $[(triphos)M(P_3X_3)]$ [M = Rh, X = S (**1**), Se (**2**); M = Ir, X = S (**3**), Se (**4**)], which have been

Chart I. Summary of Structure Types Obtained in the Reaction of P_4X_3 with Various Metal Complexes



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