Mechanism for Thermal Generation of Transient Rhenium(0) Radicals. Reaction of a (Triphenylmethyl)rhenium Complex with Two-Electron Ligands

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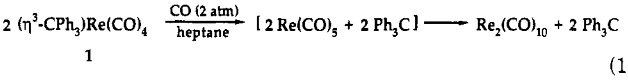
Reaction of (η^3-CPh_3)$Re(CO)_4$ (1) with 2 equiv of the cage phosphite 1-methyl-4-phospha-3,5,8-trioxabicyclo[2.2.2]octane (MPTB) results in formation of *mer-trans*-$Re(CO)_3(MPTB)_2$(4-(diphenylmethylene)cyclohexa-2,5-diene) (**2a**). In solution at 233 K, **2a** isomerizes to the facial-cis isomer **2b**. At higher temperatures, **2a** and **2b** decompose via metal–alkyl bond homolysis to give Ph_3C radicals and the transient Re(0) radicals $Re(CO)_3(MPTB)_2$, which decompose. The reactivity of (η^3-CPh_3)$Re(CO)_4$ toward other neutral two-electron phosphorus donor ligands is similar, but the corresponding rhenium–alkyl products $Re(CO)_3P_2$(4-(diphenylmethylene)cyclohexa-2,5-diene) could not be isolated from solution. Instead, they were derivatized with use of Ph_3SnH or CCl_4 to the corresponding hydrides or chlorides. Several mechanisms that could account for the observed reactivity of 1 with phosphines and phosphites to generate transient Re(0) radicals are discussed.

Introduction

Interest in the study of 17-electron metal complexes has grown in recent years. This is due, in part, to the increasing body of evidence which suggests that these labile species act as intermediates in a variety of reactions.[1] Several different strategies have been used to generate metal-centered radicals, such as metal–metal bond homolysis under photolytic[2] or thermal[3] conditions and one-electron oxidation or reduction of diamagnetic compounds[4] with use of electrochemical or chemical methods. We have utilized a different approach to the synthesis of 17-electron species involving homolysis of a weak metal–carbon σ bond under mild thermal conditions.

Recently, we reported the synthesis of (η^3-CPh_3)$Re(CO)_4$ (1), which is a thermal precursor for the transient radical $Re(CO)_5$.[5] When treated with carbon monoxide, 1 is converted to $Re_2(CO)_{10}$, via formation of $Re(CO)_5$, which readily dimerizes (eq 1). We have extended this work to other two-electron ligands and report here our results concerning the reactivity of 1 toward small phosphine and phosphite ligands.



$$\underset{\mathbf{1}}{2\,(\eta^3\text{-}CPh_3)Re(CO)_4} \xrightarrow[\text{heptane}]{\text{CO (2 atm)}} [2\,Re(CO)_5 + 2\,Ph_3C] \longrightarrow Re_2(CO)_{10} + 2\,Ph_3C \qquad (1)$$

Experimental Section

Reactions were performed under a nitrogen atmosphere with use of standard Schlenk techniques unless otherwise noted. Heptane was distilled from potassium benzophenone ketyl. Benzene and tetrahydrofuran were dried over sodium–potassium benzophenone ketyl in evacuated vessels. Methylene chloride was distilled from 10% sodium–lead alloy and stored over activated molecular sieves in vacuo. Deuteriated solvents tetrahydrofuran-d_8 and benzene-d_6 were dried over sodium–potassium benzophenone ketyl and stored in vacuo. Deuteriated solvents dichloromethane-d_2 and cyclohexane-d_{12} were stored in evacuated vessels over activated molecular sieves. The cage phosphite 1-methyl-4-phospha-3,5,8-trioxabicyclo[2.2.2]octane (MPTB) was prepared according to a reported synthesis.[6] (*Caution*: MPTB is quite toxic and should be handled accordingly.) (η^3-$CPh)_3Re(CO)_4$ was synthesized as previously reported.[5] Triphenylmethyl radical was synthesized by using a modification of a previously reported method.[7] Carbon tetrachloride (99% ^{13}C enriched), obtained from Cambridge Isotope Laboratories, was diluted to 20% ^{13}C label with natural-abundance carbon tetrachloride and stored in an evacuated vessel. Carbon monoxide (99% ^{13}C enriched) was obtained from Merck and stored over activated molecular sieves. All other reagents were obtained from commercial sources and used without further purification. Infrared spectra were recorded on a Nicolet 5-SX FT-IR instrument. NMR experiments were performed on a Bruker WM250 or WM500 spectrometer. Elemental analyses were performed by Galbraith Analytical Laboratory.

Preparation of $Re(CO)_3(MPTB)_2$(4-(diphenylmethylene)cyclohexa-2,5-diene) (2). A solution of (η^3-CPh_3)$Re(CO)_4$ (1; 153 mg, 0.28 mmol) in 15 mL of heptane was stirred and cooled to 0 °C. A solution of MPTB (87 mg, 0.56 mmol) in 8 mL of heptane was added over a 5-min period. During this time, a dark orange precipitate formed. After 30 min of stirring, the supernatant was removed. The precipitate was washed with 5 mL of heptane and dried in vacuo; yield 176 mg (0.22 mmol, 78% based on 1). Anal. Calcd for $ReC_{32}H_{33}O_9P_2$: C, 47.47; H, 4.11; P, 7.65. Found: C, 47.35; H, 4.30; P, 7.88. ^1H NMR (250 MHz, 203 K, THF-d_8): δ 7.3–7.0 (m, 10 H, phenyl), 6.38 (d of d, J = 9.2, 4.1 Hz, 2 H, vinylic), 6.13 (d, J = 9.2 Hz, 2 H, vinylic), 4.13 (s, 6 H, MPTB CH_2), 3.6 (under solvent peak, 1 H, allylic), 0.72 (s, 3 H, MPTB CH_3). At 233 K, the following new peaks appear in the ^1H NMR spectrum: δ 6.56 (d of d, J = 9.2, 4.1 Hz, 2 H, vinylic), 5.98 (d, J = 9.2 Hz, 2 H, vinylic), 4.20 (s, 6 H, MPTB CH_2), 0.77 (s, 3 H, MPTB CH_3). When the sample was warmed to room temperature, peaks for **2a** and **2b** disappeared and new resonances corresponding to the dimer of the triphenylmethyl radical, 1-(diphenylmethylene)-4-(triphenylmethyl)-2,5-cyclohexadiene, appeared corresponding to the ^1H NMR spectrum for an authentic sample. ^1H NMR (250 MHz, benzene-d_6): δ 7.30–7.00 (m, 25 H, phenyl), 6.43 (d of d, J = 10,

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2 Hz, 2 H, vinylic), 5.91 (d of d, J = 10, 4 Hz, 2 H, vinylic), 4.92 (m, 1 H, allylic).

^{13}CO Enrichment of 1 and Conversion to 2. A solution of 1 (50 mg, 0.092 mmol) in 50 mL of heptane was degassed in a tube fitted with a high-vacuum Teflon stopcock. ^{13}C-enriched CO (99% ^{13}CO) was introduced into the tube to a final pressure of 200 Torr. The tube was sealed, and the solution was stirred for 24 h, with use of IR spectroscopy to monitor the extent of ^{13}CO incorporation. The solution was filtered and concentrated to one-third its original volume. MPTB (29 mg, 0.19 mmol) was added. The resulting precipitate of 2 was washed with heptane and dried in vacuo. ^{13}C NMR (62.89 MHz, 203 K, THF-d_8): δ 15.4 (s, 1 C, MPTB CH_3), 33.0 (t, J_{PC} = 17 Hz, 1 C, allylic), 76.2 (s, 3 C, MPTB CH_2), 118.3 (s, 2 C, vinyl), 125.6 (s, 2 C, para), 128.4 (s, 4 C, ortho), 131.9 (s, 4 C, meta), 145.4 (s, 2 C, ipso), 146.7 (s, 2 C, vinyl), 187.3 (t, J_{PC} = 10 Hz, 1 C, CO)), 193.1 (t, J_{PC} = 14 Hz, 2 C, CO).

Reaction of 1 with PMe_3. PMe_3 (20 μL, 0.20 mmol) was added to a solution of 1 (50 mg, 0.01 mmol) in 3 mL of heptane. The solution immediately turned bright orange, and a deep orange precipitate formed over a 5-min period. The suspension then began to lose its color; after 12 h of stirring, the precipitate had dissolved and the solution was light yellow. An IR spectrum of the heptane solution indicated the presence of multiple decomposition products: ν_{CO} 2015 (w), 2010 (w), 1895 (w), 1932 (m), 1919 (s), 1905 (m), 1883 (w), 1873 (m), 1863 (m), 1850 (m), 1843 (w) cm^{-1}. The sole organic product formed was identified as Ph_3CH by ^1H NMR spectroscopy (250 MHz, benzene-d_6): δ 7.1 (m, 15 H, Ph_3CH), 5.41 (s, 1 H, Ph_3CH).

Reaction of 1 with $P(OMe)_3$. $P(OMe)_3$ (20 μL, 0.17 mmol) was added to a solution of 1 (31 mg, 0.055 mmol) in 3 mL of heptane. The solution turned from yellow to orange-yellow over a 10-min period. The solution was stirred for 12 h; during this time a white precipitate of $Ph_3COOCPh_3$ formed and the solution turned colorless. ^1H NMR (250 MHz, benzene-d_6): δ 7.39–7.35 (m, 12 H, ortho), 7.04–7.02 (m, 18 H, meta, para). The IR spectrum of the supernatant consisted of four bands in the carbonyl stretching region: 1970 (m), 1943 (s), 1909 (w), 1882 (s) cm^{-1}.

Reaction of 1 with 1,2-(Diphenylphosphino)ethane (diphos). A Schlenk tube containing 1 (33 mg, 0.061 mmol) and diphos (26 mg, 0.065 mmol) was evacuated. Benzene (2 mL) was transferred in under vacuum. The initial yellow solution became orange, and the reaction mixture was stirred for 24 h. The solvent was removed in vacuo; an IR spectrum of the resulting residue dissolved in CH_2Cl_2 showed the presence of a carbonyl-containing compound, which was identified as $Re_2(CO)_6(diphos)_2$ on the basis of elemental analysis. IR (CH_2Cl_2): ν_{CO} 1995 (w), 1959 (s, br) cm^{-1}. Anal. Calcd for $Re_2C_{58}H_{48}O_6P_4$: C, 52.09; H, 3.62. Found: C, 50.93; H, 3.66. The organic product was identified as Ph_3CH by ^1H NMR spectroscopy.

Reaction of 2 with Ph_3SnH. A Schlenk flask containing 24 mg of 2 (0.045 mmol) was evacuated. CH_2Cl_2 (10 mL) was transferred in under vacuum and frozen. The solution was warmed to −78 °C, and an excess of Ph_3SnH (60 mg, 0.171 mmol) was added under a nitrogen atmosphere. The solution was stirred and kept at −78 °C for 2 days. Over this time, the solution turned from orange to colorless. The solvent was removed in vacuo, leaving a colorless residue. IR (benzene): ν_{CO} 2036 (w), 1966 (s, br), 1945 (w) cm^{-1}. The ^1H NMR spectrum of the residue, dissolved in benzene-d_6, showed resonances corresponding to Ph_3CH and *mer-trans*-$Re(CO)_3(MPTB)_2H$: δ 3.43 (s, 6 H, MPTB CH_2), −0.42 (s, 3 H, MPTB CH_3), −5.8 (t, J = 25 Hz, 1 H, Re–H). When the reaction was performed at room temperature, a mixture of the *mer-trans* and *fac-cis* isomers of $Re(CO)_3(MPTB)_2H$ was obtained in the ratio 7.5:1. ^1H NMR (250 MHz, benzene-d_6): δ −5.4 (t, J = 30 Hz, 1 H, *fac-cis* Re–H), −5.8 (t, J = 25 Hz, 1 H, *mer-trans* Re–H).

Reaction of 2 with Bu_3SnD. Bu_3SnD (12 μL, 0.042 mmol) was added to a solution of 2 (17 mg, 0.0210 mmol) in 1 mL of benzene at ambient temperature. The orange solution became colorless over a 2-min period. An IR spectrum of the solution showed the presence of both the *mer-trans* and *fac-cis* isomers of $Re(CO)_3(MPTB)_2H$, with the mer-trans species the major product. IR (benzene): ν_{CO} 2039 (w), 1964 (s, br), 1944 (w) cm^{-1}. The ^2H NMR spectrum (76.78 MHz, benzene) of the product mixture contained resonances corresponding to Ph_3CD at δ 5.35, *fac-cis*-$Re(CO)_3(MPTB)_2D$ at δ −5.41, and *mer-trans*-$Re(CO)_3(MPTB)_2D$ at δ −5.85. No incorporation of deuterium into the phenyl rings of Ph_3CH was observed.

Reaction of 1 with 1 Equiv of MPTB in the Presence of Ph_3SnH. MPTB (7.6 mg, 0.051 mmol) and Ph_3SnH (56 mg, 0.16 mmol) were dissolved in 4 mL of heptane. The solution was cooled to 0 °C, and 1 (26 mg, 0.048 mmol) was added. A white precipitate of $(Ph_3Sn)_2$ formed over a 10-min period; after 30 min of stirring, the precipitate was allowed to settle, the supernatant was filtered, and the solvent was removed in vacuo. The ^1H NMR spectrum (250 MHz, benzene-d_6) of the resulting colorless residue showed a doublet in the hydride region at δ −5.4 with a J_{PH} coupling constant of 30 Hz, consistent with formation of *cis*-$Re(CO)_4(MPTB)H$ (identified by comparison to ^1H NMR data[8] for *cis*-$Re(CO)_4P(OPh)_3H$ in benzene-d_6: δ −5.86, d, J_{PH} = 32 Hz). IR (heptane): ν_{CO} 2095 (w), 2005 (m), 1995 (s), 1885 (s) cm^{-1} (compare to IR data[8] for *cis*-$Re(CO)_4P(OPh)_3H$ in cyclohexane: 2088 (m), 2003 (s), 1989 (vs), 1983 (s, sh) cm^{-1}).

Reaction of 1 with PMe_3 in the Presence of Ph_3SnH. Ph_3SnH (230 mg, 0.65 mmol) and PMe_3 (52 mg, 0.69 mmol) were dissolved in 15 mL of heptane, and 1 (150 mg, 0.28 mmol) was added. The resulting yellow solution was stirred; over a 30-min period, a white precipitate of $(Ph_3Sn)_2$ formed and the supernatant became colorless. The heptane solution was filtered, concentrated, and cooled to −45 °C. A fine white precipitate formed, which contained a mixture of *mer-trans* and *fac-cis* isomers of $Re(CO)_3(PMe_3)_2H$, yield 104 mg, 88% (based on 1). ^1H NMR (250 MHz, benzene-d_6): δ 1.34 (t, J = 2 Hz, 9 H, *mer-trans* PMe_3), 1.10 (virtual triplet, 9 H, *fac-cis* PMe_3), −5.84 (t, J = 21 Hz, 1 H, *mer-trans* Re–H), −4.79 (t, J = 28 Hz, 1 H, *fac-cis* Re–H) (compare to literature value[8] for *mer-trans*-$Re(CO)_3(PEt_3)_2H$: δ −6.53, t, J = 20 Hz). IR (heptane): ν_{CO} 2010 (m), 1920 (m), 1910 (s) cm^{-1} (compare to literature value[8] for *mer-trans*-$Re(CO)_3(PEt_3)_2H$: 1906 (s) cm^{-1}).

Reaction of 1 with $P(OMe)_3$ in the Presence of Ph_3SnH. Ph_3SnH (25 mg, 0.102 mmol) and $P(OMe)_3$ (15 μL, 0.13 mmol) were dissolved in 5 mL of heptane; 1 (25 mg, 0.046 mmol) was then added. After 5 min a white precipitate of $(Ph_3Sn)_2$ began to form. The suspension was stirred for 1 h. The supernatant was filtered, and the solvent was removed in vacuo. The resulting white residue containing both *mer-trans*- and *fac-cis*-$Re(CO)_3[P(OMe)_3]_2H$ in the ratio 4.3:1 (as well as Ph_3CH) was dissolved in benzene-d_6. ^1H NMR (250 MHz, benzene-d_6): δ −5.90 (t, J = 30 Hz, 1 H, *fac-cis* Re–H), −6.32 (t, J = 25 Hz, 1 H, *mer-trans* Re–H). IR (benzene): ν_{CO} 2028 (w), 1950 (s, br), 1935 (w) cm^{-1}.

Reaction of 1 with diphos in the Presence of Ph_3SnH. (η^3-CPh_3)$Re(CO)_4$ (7 mg, 0.013 mmol), diphos (5.6 mg, 0.014 mmol), and Ph_3SnH (10 mg, 0.028 mmol) were loaded into an NMR tube equipped with a high-vacuum Teflon stopcock. Benzene-d_6 was transferred in under vacuum, and the tube was flame-sealed. When it thawed, the initial yellow solution became colorless over a 45-min period. The ^1H NMR spectrum (250 MHz, benzene-d_6) exhibited a hydride resonance corresponding to *fac-cis*-$Re(CO)_3(diphos)H$: δ −5.1 (t, J_{PH} = 26 Hz, 1 H) (literature value[8] δ −5.2, t, J_{PH} = 26 Hz). The organic product was identified as Ph_3CH.

Reaction of 2 with CCl_4. A sample of 2 (8 mg, 0.010 mmol) was loaded into a tube fitted with a high-vacuum Teflon stopcock and degassed. CCl_4 (0.1 mL, 0.10 mmol) and 2 mL of benzene were transferred in under vacuum. When it thawed, the solution lightened from deep orange to light yellow, accompanied by precipitation of *mer-trans*-$Re(CO)_3(MPTB)_2Cl$ as an off-white powder. The solid product was washed with 5 mL of heptane and dried in vacuo. Anal. Calcd for $ReC_{13}H_{18}O_9P_2Cl$: C, 25.94; H, 3.01. Found: C, 24.92; H, 2.96. IR (CH_2Cl_2): ν_{CO} 2087 (w), 1996 (s), 1937 (m) cm^{-1}. The solution, containing the organic products **4a** and **4b**, was removed to a Schlenk tube; the solvent was removed in vacuo. ^1H NMR (500 MHz, cyclohexane-d_{12}): δ 4.0 (t of t, J = 4, 2 Hz, 1 H), 4.6 (d, J = 8 Hz, 1 H), 5.7 (m, 1 H), 6.1 (d of d, J = 8, 4 Hz, 2 H), 6.2 (m, 1 H), 6.3 (m, 1 H), 6.6 (d, J = 8 Hz, 1 H), 6.7 (d of d, J = 8, 2 Hz, 2 H), 7.0–7.5 (20 H). The assignment of resonances (Table II) is based on a series of selective ^1H decoupling experiments.

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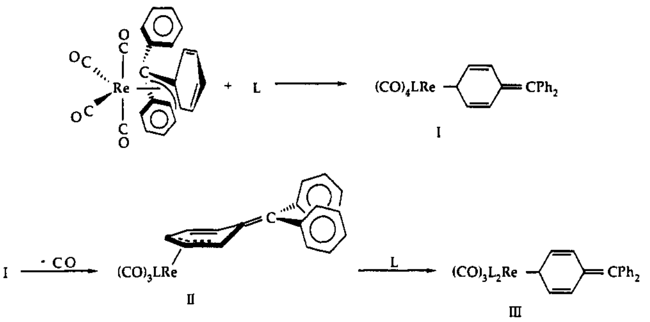
Scheme I

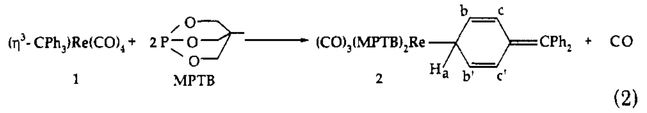


Reaction of 1 with 1 Equiv of MPTB in the Presence of CCl_4. MPTB (8.6 mg, 0.055 mmol) and CCl_4 (0.1 mL, 1.03 mmol) were dissolved in 5 mL of heptane and cooled to 0 °C; 1 (30 mg, 0.055 mmol) was then added. The initial clear yellow solution became cloudy over a 15-min period. The precipitate was identified as $Re(CO)_4(MPTB)Cl$ on the basis of its IR spectrum. IR (CH_2Cl_2): ν_{CO} 2125 (w), 2020 (s, br), 1955 (m) cm^{-1} (compared to IR data for $Re(CO)_4PEt_3Cl$ in cyclohexane:[9] 2102 (w), 1997 (s), 1987 (m), 1943 (m) cm^{-1}). The light yellow supernatant was filtered, and the solvent was removed in vacuo to give a residue containing **4a** and **4b**.

Reaction of 1 with CO in the Presence of ^{13}C-Enriched CCl_4. A sample of 1 (20 mg, 0.037 mmol) was degassed in an NMR tube equipped with a high-vacuum Teflon stopcock. CCl_4 (20% enriched in ^{13}C, 35 mg, 0.110 mmol) was transferred in under vacuum followed by 0.5 mL of cyclohexane-d_{12}. The tube was pressurized with CO (3 atm). Over a 10-h period, a white precipitate of $Re(CO)_5Cl$ formed. The tube was then flame-sealed. ^1H NMR spectral data recorded were identical with those reported above for compounds **4a** and **4b**, except that additional splittings due to ^{13}C–H coupling were observed on the resonances corresponding to the protons on the two carbons adjacent to the CCl_3 groups. ^{13}C NMR (125.78 MHz, cyclohexane-d_{12}): δ 57.7 (1 C), 59.4 (1 C, 103.2 (1 C, 105.4 (1 C), 123.4 (1 C), 124.7 (2 C), 125.4 (1 C), 127.8 (2 C), 128.4 (4 C), 129.6 (s, 1 C), 130.5 (1 C), 130.6 (2 C), 131.3 (4 C), 131.4 (4 C), 131.9 (2 C), 132.0 (4 C), 142.0 (2 C), 143.8 (2 C). The assignment of resonances (Table II) is based on results of a heteronuclear shift correlation experiment[10] and comparison with compounds having similar structures.

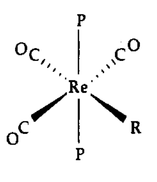
Results and Discussion

Preparation and Characterization of $Re(CO)_3$-$(MTPB)_2$(4-(diphenylmethylene)cyclohexa-2,5-diene) (2). Addition of 2 equiv of the cage phosphite MPTB to a solution of (η^3-CPh_3)$Re(CO)_4$ (1) resulted in immediate formation of a deep orange precipitate of $Re(CO)_3$-$(MPTB)_2$(4-(diphenylmethylene)cyclohexa-2,5-diene) (2) (eq 2). Addition of 1 equiv of MPTB gave 50% conversion to 2, with no monophosphine-substituted products observed, indicating that addition of the second equivalent of phosphine occurred more rapidly than the first. When the reaction was carried out in THF-d_8 at 203 K, 2 was the only product observed by ^1H NMR spectroscopy; no tetracarbonyl monophosphine intermediate was detected.[11] Upon exposure to air, solid samples of 2 quickly decolorized. The compound was also unstable in solution at room temperature. However, we were able to obtain NMR spectra at low temperatures for characterization purposes.

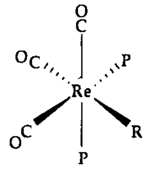


(2)

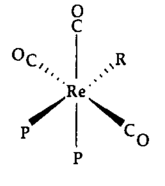
The ^1H NMR spectrum of 2 at 203 K (250 MHz, THF-d_8) exhibits a doublet of doublets at δ 6.38, corresponding to protons H_b and $H_{b'}$, and a doublet at δ 6.13, corresponding to protons H_c and $H_{c'}$. The resonance due to H_a, obscured by residual protio tetrahydrofuran at δ 3.6, was confirmed by selective ^1H decoupling experiments. The stereochemistry at rhenium was determined to be meridional-trans, as in **2a**, on the basis of ^{13}C NMR data collected (62.89 MHz, THF-d_8, 203 K) for 2 with ^{13}C-enriched carbonyl groups. There are two carbonyl resonances in the ratio 2:1, each coupled to two equivalent phosphines. The alkyl carbon atom attached to rhenium is also coupled to two equivalent phosphines. When the sample was warmed to 233 K, a second set of resonances having the same splitting pattern, but at higher field, appeared in the ^1H NMR spectrum, indicating formation of a second isomer of 2. On the basis of subsequent trapping reactions (vide infra), we tentatively assign the configuration at rhenium to be the facial-cis isomer **2b**. Over a 30-min period, the resonances due to **2b** grew in and those due to **2a** diminished until the two sets had roughly equal intensity. No further resonances appeared in the spectrum until the solution was warmed to 273 K and decomposition occurred. This facile isomerization process observed at low temperatures is quite rare for six-coordinate metal complexes, which are normally configurationally stable.[12,13] It is clear that free radicals cannot be involved because no rhenium dimers were observed while isomerization was occurring. One possible explanation for this phenomenon is that the metal–alkyl bond is weak and is easily homolyzed to give the solvent cage radical pair $Re(CO)_3(MPTB)_2{}^{\bullet}R^{\bullet}$. Within the cage, the five-coordinate rhenium center can isomerize and recombine with $R^{\bullet}$ to give the second isomer seen before diffusing out of the cage.[12] If this mechanism is operative, a third isomer, **2c**, could also be formed. We have observed only two isomers in these low-temperature studies and in related trapping experiments (vide infra). However, if the isomer **2c** were thermodynamically disfavored, it would not be formed in any of the reactions studied.



2a



2b



2c

Reaction of (η^3-CPh_3)$Re(CO)_4$ (1) with other neutral two-electron phosphorus ligands such as $P(OMe)_3$, PMe_3, and diphos (1,2-bis(diphenylphosphino)ethane) under the same reaction conditions resulted in formation of orange compounds that rapidly decomposed in heptane to give multiple rhenium-containing products.

On the basis of these results, we propose the mechanism depicted in Scheme I to account for the observed reactivity of 1 toward small phosphines and phosphites. In the first step, 1 equiv of ligand adds to the rhenium center in an associative fashion to give I. On the basis of results of trapping reactions using carbon tetrachloride[14] (vide infra),

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[9] Bucknor, S.; Cotton, F. A.; Falvello, L. R.; Reid, A. H., Jr.; Schmulbach, C. D. *Inorg. Chem.* **1986**, *25*, 1021–1027.

[10] Bax, A.; Morris, G. *J. Magn. Reson.* **1981**, *42*, 501–505.

[11] When the reaction of 1 with 1 equiv of MPTB was carried out in the presence of Ph_3SnH, *cis*-$Re(CO)_4(MPTB)H$ was the sole rhenium-containing product observed: ^1H NMR (250 MHz, benzene-d_6) δ −5.45 (d, J_{PH} = 30 Hz).

[12] Muetterties, E. L. *Acc. Chem. Res.* **1969**, *3*, 266–273.

[13] (a) Vancea, L.; Pomeroy, R. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1976**, *98*, 1407–1413. (b) Vancea, L.; Graham, W. A. G. *J. Organomet. Chem.* **1977**, *134*, 219–227. (c) Vancea, L.; Bennet, M. J.; Jones, C. E.; Smith, R. A.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1508–1514.

we believe that the triphenylmethyl group rearranges to a quinoid structure with the addition of the first equivalent of ligand. Intermediate I can then lose carbon monoxide to form II; although there is no direct evidence for the structure of II, it seems more plausible to invoke a complex in which the rhenium is bound to three carbons of the phenyl ring rather than a complex having a structure similar to 1, which would require more extensive rearrangement. Intermediate II reacts rapidly with a second equivalent of ligand to give III, which can be isolated for L = MPTB. In solution at ambient temperature, III undergoes metal–alkyl bond homolysis to generate $Re(CO)_3(MPTB)_2$ radicals, which decompose in solution.

Trapping Reactions Using Ph_3SnH. Due to the instability of these rhenium–alkyl complexes and the subsequent radicals formed, we were interested in intercepting the rhenium center prior to decomposition using a trapping agent which would give a more tractable product that could be routinely characterized. Trialkyltin hydrides have been used in a number of studies for derivitization of 17-electron metal radicals to the corresponding metal–hydride complexes.[15,16] The highfield shift characteristic of metal hydrides seen in the ^1H NMR spectrum, combined with coupling information, provides a straightforward method for determining the arrangement of ligands around a metal center. Also, such $Re(CO)_3P_2H$ complexes are soluble in hydrocarbons such as heptane and benzene, suitable solvents for obtaining IR spectral data.

Addition of Ph_3SnH to a dichloromethane solution of **2** at room temperature resulted in immediate formation of $Re(CO)_3(MPTB)_2H$ (**3**; eq 3). The ^1H NMR spectrum

$$2 + 2\,\text{Ph}_3\text{SnH} \longrightarrow \underset{3}{\text{Re(CO)}_3\text{(MPTB)}_2\text{H}} + \text{Ph}_3\text{CH} + (\text{Ph}_3\text{Sn})_2 \qquad (3)$$

of the product mixture exhibits two triplets in the hydride region (δ −5.8, J = 26 Hz; δ −5.4, J = 30 Hz) in the ratio 7.5:1, corresponding to two isomers of **3**, each having equivalent phosphines. The IR spectrum of the products in benzene consists of a weak band at 2036 cm^{-1}, a very strong broad band at 1966 cm^{-1}, and a weak band at 1945 cm^{-1}. This is consistent with a mixture in which the *mer-trans* isomer is the major component with a small amount of *fac-cis* isomer present.[8] When the same reaction was carried out at −78 °C, only the triplet at δ −5.8, corresponding to the *mer-trans* isomer, was observed in the ^1H NMR spectrum.

Similar experiments were performed by adding **1** to solutions containing various ligands and Ph_3SnH (eq 4).

$$1 + \begin{matrix}2\text{L}\\ \text{or}\\ \overset{\frown}{\text{L L}}\end{matrix} + \text{Ph}_3\text{SnH} \longrightarrow \begin{matrix}\text{Re(CO)}_3\text{L}_2\text{H}\\ \text{or}\\ \text{Re(CO)}_3(\overset{\frown}{\text{L L}})\text{H}\end{matrix} + \text{Ph}_3\text{CH} + 1/2(\text{Ph}_3\text{Sn})_2 \qquad (4)$$

$L = PMe_3, P(OMe)_3$

$\overset{\frown}{\text{L L}}$ = DIPHOS

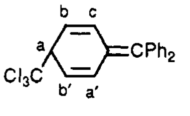
^1H NMR spectral data for the resulting rhenium hydrides are collected in Table I. On the basis of NMR data for compounds whose stereochemistry is known due to ligand constraints (e.g. *fac-cis*-$Re(CO)_3(diphos)H$[8] and *mer-trans*-$Re(CO)_3(PCy_3)_2H$[16]), the assignment of hydride resonances for compounds with two possible isomers was made. In each case, the *fac-cis* hydride complexes give rise to triplets at lower field with larger J_{PH} coupling constants than the corresponding *mer-trans* isomers. IR spectra consist of three bands of equal intensity for the *fac-cis* isomers[17] and a single strong band for *mer-trans* isomers.[8] The ratio of isomers depended on the temperature at which the reaction was carried out. At −78 °C, the *mer-trans* isomer predominated in all cases (except for $Re(CO)_3(diphos)H$, which must have a *fac-cis* arrangement). When the reaction was performed at ambient temperature, the relative amount of the *fac-cis* isomer increased. Additional heating of product mixtures did not alter the final ratios.

Table I. ^1H NMR Data for $Re(CO)_3P_2H$ Complexes[a]

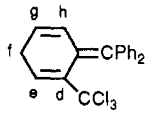
compd	*fac-cis* δ(Re–H)	*fac-cis* J_{PH}, Hz	*mer-trans* δ(Re–H)	*mer-trans* J_{PH}, Hz
$Re(CO)_3(diphos)H$	−5.14	26		
$Re(CO)_3(PCy_3)_2H$[b]			−6.23	20
$Re(CO)_3(PMe_3)_2H$	−4.79	28	−5.84	20
$Re(CO)_3[P(OMe)_3]_2H$	−5.90	30	−6.32	25
$Re(CO)_3(MPTB)_2H$	−5.39	30	−5.79	26

[a] In benzene-d_6. [b] Data from ref 16.

Table II. ^1H and ^{13}C NMR Data for 4a and 4b[a]



4a

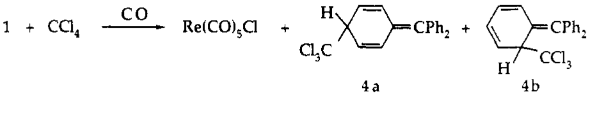


4b

position	^1H chem shift, ppm (J, Hz)	^{13}C chem shift, ppm
a	4.0 tott (4, 2)	59.4
b, b′	6.1 d of d (8, 4)	124.7
c, c′	6.7 d of d (8, 2)	131.9
d	4.6 d (8)	57.7
e	6.2 m	125.4
f	6.3 m	129.6
g	5.7 m	123.4
h	6.6 d (8)	130.5

[a] in cyclohexane-d_{12}.

Trapping Reactions Using CCl_4. In earlier studies, carbon tetrachloride was used to intercept radicals formed in the reaction of **1** with carbon monoxide (eq 5).[5] We



predicted that the $Re(CO)_5$ produced in the reaction would react readily with carbon tetrachloride to give the observed product $Re(CO)_5Cl$. Previous workers have shown that triphenylmethyl radicals react with carbon tetrachloride to give 1,1,1-trichloro-2,2,2,-triphenylethane.[18] Thus, we were surprised to observe formation of two new organic products, **4a** and **4b**. ^{13}C NMR data for a sample of **4a** and **4b** prepared by reaction of **1** with ^{13}C-enriched CCl_4 under an atmosphere of carbon monoxide contained singlets at δ 103.2 and 105.4, corresponding to the trichloromethyl carbon in each.

The same organic products were observed in the reaction of **2** with carbon tetrachloride; the IR spectrum shows a

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(14) When the reaction of 1 with 1 equiv of MPTB was carried out in the presence of CCl_4, **4a** and **4b** were the only organic products formed.

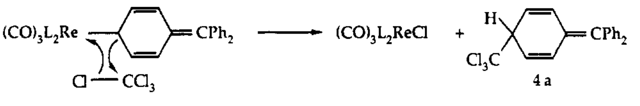
(15) (a) McCullen, S. B.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 7496–7500. (b) Cooley, N. A.; Watson, K. A.; Fortier, S.; Baird, M. C. *Organometallics* **1986**, *5*, 2563–2565. (c) Hankel, J. M.; Lee, K.-W.; Rushman, P.; Brown, T. L. *Inorg. Chem.* **1986**, *25*, 1852–1856. (d) Kuchynka, D. J.; Amatore, C.; Kochi, J. K. *J. Organomet. Chem.* **1987**, *328*, 133–154.

(16) Walker, H. W.; Rattinger, G. B.; Belford, R. L.; Brown, T. L. *Organometallics* **1983**, *2*, 775–776.

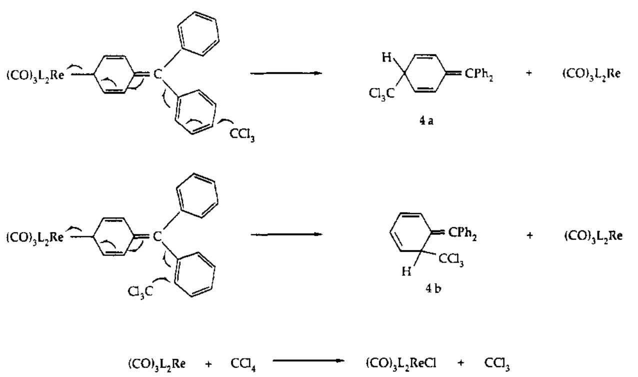
(17) In these product mixtures, one or both of the lower frequency ν_{CO} stretching modes corresponding to the *fac-cis* isomer are often obscured by the single strong band due to the *mer-trans* isomer.

(18) Hey, D. H.; Peters, J. *J. Chem. Soc.* **1960**, 79–88.

Scheme II



Scheme III



three-band pattern in the carbonyl stretching region (2087 (w), 1996 (s), 1937 (m) cm^{-1}) which indicates that only the *mer-trans*-Re(CO)$_3$(MPTB)$_2$Cl isomer was formed (eq 6).

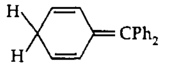
$$2 + CCl_4 \longrightarrow \text{mer-trans Re(CO)}_3\text{(MPTB)}_2\text{Cl} + 4a + 4b \qquad (6)$$

The structures for **4a** and **4b** were deduced on the basis of data from a series of selective ^{1}H NMR decoupling experiments in conjunction with a ^{1}H–^{13}C heteronuclear shift correlation experiment; a summary of spectral assignments is given in Table II. There is little precedent for such compounds in the literature;[19] thus, it is interesting to speculate on possible mechanisms for their formation.

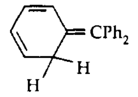
Mechanistic Considerations. In these trapping reactions, it is clear that carbon tetrachloride is not acting as an "innocent" radical scavenger, intercepting only free radicals. The organic products generated in these reactions are inconsistent with initial formation of free radicals. Thus, it is likely that carbon tetrachloride is interacting in some way with the 18-electron species Re(CO)$_3$L$_2$R (R = 4-(diphenylmethylene)cyclohexa-2,5-diene). Two possible mechanisms that are consistent with the results obtained in this study are depicted in Schemes II and III.

Scheme II shows carbon tetrachloride reacting in a concerted fashion with Re(CO)$_3$L$_2$R to give the corresponding rhenium chloride and **4a**. However, this cannot be the only mechanism, because it accounts for formation of **4a** and not **4b**. In Scheme III, reaction of carbon tetrachloride with Re(CO)$_3$L$_2$R occurs via a chain mechanism with a CCl$_3$ radical attacking either the ortho or para positions of the phenyl rings. Subsequent electronic rearrangement gives rise to either **4a** or **4b** and a rhenium radical, which reacts quickly with another molecule of carbon tetrachloride to give the resulting rhenium chloride and a CCl$_3$ radical. In the reaction of **2** with carbon tetrachloride, where only the *mer-trans* product is seen, isomerization of Re(CO)$_3$(MPTB)$_2$ must be slower than the trapping reaction. Since the reaction is performed with use of a large excess (~10-fold excess) of carbon tetrachloride, which is known to react with Re(CO)$_5$ radicals at diffusion-controlled rates ($k = 3.9 \times 10^7$ M^{-1} s^{-1}),[20] this is not an unreasonable assumption. If the reaction proceeds entirely by the mechanism shown in Scheme III, the expected ratio of **4a**:**4b** would be 1:2 on the basis of the relative number of para and ortho sites (assuming no steric or electronic preferences). The observed ratio of 5:4 suggests that this is not the only operative mechanism and that the products are formed by more than one route.

It is unclear from the observed products formed in the reaction of Re(CO)$_3$L$_2$R (R = 4-(diphenylmethylene)cyclohexa-2,5-diene) with triphenyltin hydride whether the hydride is intercepting an 18-electron species in a manner analogous to that for carbon tetrachloride or whether it is trapping free radicals. If attack occurred via a pathway similar to those depicted in Schemes II and III, the resulting hydrocarbons **5a** and **5b** would probably be quite unstable and would readily rearrange to triphenylmethane.[21] In order to test this possibility, **2** was treated with tributyltin deuteride under the same reaction conditions used for reaction with triphenyltin hydride. If **5a** and **5b** were formed and did subsequently rearrange to give triphenylmethane, incorporation of deuterium into the para and meta ring positions should be observed. The ^{2}H NMR spectrum of the resulting product mixture contained resonances corresponding to Ph$_3$C–D and both *fac-cis* and *mer-trans* isomers of Re(CO)$_3$(MPTB)$_2$–D. No resonances were observed in the aromatic region. Thus, it seems likely that the tin hydrides are indeed reacting with free radicals.



5a



5b

Conclusion

In this study we have examined the behavior of (η^3-CPh$_3$)Re(CO)$_4$ (**1**) toward small phosphines and phosphites. We have found that **1** reacts readily with a variety of neutral two-electron phosphorus donor ligands to give unstable rhenium–alkyl complexes. These compounds decompose to liberate highly reactive Re(0) radicals. In our attempts to derivatize these radicals with the commonly used radical scavenging agent carbon tetrachloride, we have found evidence which suggests that it reacts directly with the rhenium–alkyl species themselves to form unexpected products. However, the trialkyltin and triaryltin hydrides appear to trap free Re(CO)$_3$L$_2$ and Ph$_3$C radicals.

In earlier work, we have demonstrated that stable Re(0) radicals with the general form Re(CO)$_3$L$_2$ can be generated by reaction of **1** and related triphenylmethyl complexes with large phosphines.[22] We are currently extending our work in this area to phosphines of intermediate size in

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[19] Gomberg proposed the existence of compounds similar to **4a**: Gomberg, M. *Ber. Dtsch. Chem. Ges.* **1909**, *42*, 406–417. Gomberg, M.; Van Slyke, D. D. *J. Am. Chem. Soc.* **1911**, *33*, 531–549. He was able to isolate one such compound, a diphenyl quinomethanol. Gomberg, M. *J. Am. Chem. Soc.* **1913**, *35*, 1035–1042. Later researchers reported the synthesis of a diphenyl quinoid compound with a diphenylmethyl group in the doubly allylic position: Bölsing, F.; Korn, K.-D. *Tetrahedron Lett.* **1971**, 3865–3868. DeTar and Long found that disproportionation of transient phenylcyclohexadienyl radicals leads to formation of compounds with structures similar to **4a** and **4b**: DeTar, D. F.; Long, R. A. J. *J. Am. Chem. Soc.* **1958**, *80*, 3865–3868.

[20] Meckstroth, W. K.; Walters, R. T.; Waltz, W. L.; Wojcicki, A.; Dorfman, L. M. *J. Am. Chem. Soc.* **1982**, *104*, 1842–1846.

[21] In the presence of a catalytic amount of acid or base, the dimer of the triphenylmethyl radical, 1-(diphenylmethylene)-4-(triphenylmethyl)-2,5-cyclohexadiene, rearranges to (*p*-benzhydrylphenyl)triphenylmethane via aromatization of the cyclohexadienyl ring: Ullman, F.; Borsum, W. *Ber. Dtsch. Chem. Ges.* **1902**, *35*, 2877–2881. Since **5a** and **5b** have structures similar to this dimer (both have protons on a doubly allylic carbon), they should also undergo acid- or base-catalyzed aromatization to give triphenylmethane.

[22] Crocker, L. S.; Heinekey, D. M.; Schulte, G. K. *J. Am. Chem. Soc.* **1989**, *111*, 405–406.

order to better understand the relationship between steric bulk and reactivity in Re(0) radicals.

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Synthesis, Structure, and Reactions of 2,2′-Bipyridyl Complexes of Tetramethyloxotungsten(VI) and Dimethyldioxotungsten(VI) and of Related Compounds

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Tetramethyl(2,2′-bipyridyl)oxotungsten(VI), $(CH_3)_4W(O)(bpy)$ (**1**), and several dialkyl complexes of the composition $R_2W(O)_2(bpy)$, where bpy = 2,2′-bipyridyl and R = CH_3 (**2**), C_2H_5 (**3**), *n*-C_3H_7 (**4**), and $CH_2C(CH_3)_3$ (**5**), were synthesized. Complexes **1**, **2**, and **4** were characterized by X-ray crystallographic analysis. Complex **1**, a new seven-coordinate organometallic complex of W(VI), has a distorted pentagonal-bipyramidal coordination geometry with oxygen and one bpy nitrogen in the apexal positions. The W=O bond length is 1.699 (4) Å. The four methyl groups show pairwise nonequivalence at near identical W–C bond lengths of 2.216 (8) Å. The compound hydrolyzes slowly with evolution of CH_4 to yield **2**. Complex **2** is isomorphous with the known corresponding molybdenum complex; its mean W=O bond lengths of 1.722 (3) Å are slightly longer, and the mean W–C bond lengths of 2.192 (2) Å are virtually identical with the corresponding bonds in $(CH_3)_2Mo(O)_2(bpy)$. The structural analysis of **4** revealed similar in-plane bond lengths and positional disorder of the *n*-propyl groups.

In our studies of organometallic derivatives of molybdenum(VI) we previously reported the synthesis, properties, and structures of compounds of composition $R_2Mo(O)_2(bpy)$, where R = alkyl, aralkyl, and aryl and bpy = 2,2′-bipyridyl,[2] by the reactions of $Br_2Mo(O)_2(bpy)$[3] with the corresponding organomagnesium bromides. We have since extended our studies to complexes of oxotungsten(VI), of which still only comparatively few organometallic derivatives are known.[4] The methylation of $W(O)Cl_4$ was previously investigated by several groups,[5,6] but only an unstable monomethyl derivative, $CH_3W(O)Cl_3 \cdot OEt_2$, and several of its adducts with mono- and bidentate ligands were obtained, none of which were structurally characterized. Wilkinson and his school recently demonstrated[7] that all four chloride ions of $W(O)Cl_4$ are displaced on reaction with CH_3MgCl in tetrahydrofuran (THF). The reaction occurs with concomitant reduction of W(VI) to W(V), however, producing the saltlike compound $[(CH_3)_4WO]_2Mg(THF)_4$. In our studies of the methylation of oxobromotungsten(VI) complexes of bpy we have obtained $(CH_3)_4W(O)(bpy)$ (**1**), a new seven-coordinate organometallic complex of oxotungsten(VI). In addition, we also prepared $(CH_3)_2W(O)_2(bpy)$ (**2**) and the higher dialkyl derivatives of the type $R_2W(O)_2(bpy)$ with R = C_2H_5 (**3**), *n*-C_3H_7 (**4**), and $CH_2C(CH_3)_3$ (**5**). The structures of **2** and **4** were determined by X-ray crystallographic methods.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 1330 infrared spectrometer. NMR spectra were recorded on a GE QE-300 instrument at 300 MHz (^1H) and on an EM 390 instrument at 90 MHz. UV–vis spectra were measured on a Beckman DU-40 spectrophotometer. Gaseous hydrocarbons formed on thermolysis or photolysis were measured by GLPC as described in ref 2a.

All commercially available inorganic reagents and chemical of "analytical" or "reagent grade" purity were used as received. Alkylmagnesium halides were prepared from freshly distilled alkyl bromides and Mg in dried and distilled THF.

The complex $Br_2W(O)_2(bpy)$ was obtained as a white solid by the reaction of $W(CO)_4(bpy)$ with Br_2 in ethanol as described in ref 3 when moist ethanol, i.e., 95–97% C_2H_5OH, was employed. When the reaction was carried out in highly dried C_2H_5OH, the reaction products were brown-to-yellow insoluble powders that on contact with water converted rapidly into $Br_2W(O)_2(bpy)$. The products approached the composition $Br_4W(O)(bpy)$, but further characterization was precluded due to their insolubility. IR spectra

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(1) Department of Chemistry, The University of Missouri, Columbia, MO 65211.

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(3) Hull, C. G.; Stiddard, M. H. B. *J. Chem. Soc., A* **1966**, 1633.

(4) (a) Kress, J. R. M.; Russell, M. J. M.; Wesolek, M. G.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1980**, 431. (b) Feinstein-Jaffe, I.; Pedersen, S. F.; Schrock, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 7176. (c) Feinstein-Jaffe, I.; Dewn, J. C.; Schrock, R. R. *Organometallics* **1985**, *4*, 1189. (d) Alt, H. G.; Hayen, H. I. *J. Organomet. Chem.* **1986**, *316*, 105. (e) Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1985**, *5*, 398. (f) Legzins, P.; Phillips, E. C.; Rettig, S. J.; Sanchez, L.; Trotter, J.; Yee, V. C. *Organometallics* **1988**, *7*, 1877. (g) Faller, J. W.; Ma, Y. *Organometallics* **1988**, *7*, 559.

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