in weakly basic media. It is noteworthy that β-hydroxy-substituted organosilanes,[25] organostannanes,[26] and organoplumbanes[26] exhibit anti elimination under acidic conditions but undergo syn elimination thermally or with base catalysis.

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Registry No. 1, 72050-15-8; 2, 65904-27-0; 3a, 85442-28-0; 3b, 85442-30-4; 4, 85442-29-1; 5, 85442-23-5; 6, 85442-24-6; 7, 85442-25-7; 8, 85442-26-8; 9, 85442-27-9.

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Formation and Characterization of the Persistent Rhenium Radical Bis(tricyclohexylphosphine)tricarbonylrhenium(0)

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Summary: The first example of a persistent rhenium(0) radical, Re(CO)$_3$(P-c-Hx$_3$)$_2$·, has been prepared and characterized in benzene solution, by extended photolysis of Re$_2$(CO)$_8$(P-c-Hx$_3$)$_2$ in the presence of excess P-c-Hx$_3$, with removal of CO. EPR, IR, and UV-visible spectra have been obtained.

Radicals of the type Re(CO)$_{5-n}$L$_n$· (L = phosphorus donor ligand) have been proposed as intermediates in the thermal and photochemical substitution reactions of HRe(CO)$_5$[1] and Re$_2$(CO)$_{10}$.[2-4] Earlier claims of stable Re(CO)$_3$L$_2$· radicals[5,6] have been shown to be incorrect; the products formed proved to be diamagnetic compounds.[4a,7,8] Recent reported attempts to produce persistent rhenium radicals have been unsuccessful.[4a] In general, formation of persistent rhenium radicals will be difficult because of the greater ease of metal–metal bond formation and greater driving force for atom abstraction from solvent as compared with manganese. We report here the first example of a persistent metal-centered substituted rhenium carbonyl radical, Re(CO)$_3$(P-c-Hx$_3$)$_2$. (P-c-Hx$_3$ = tricyclohexylphosphine). The unique stability of this radical is ascribable to the large cone angle of the phosphine.[9]

Table I. EPR Spin-Hamiltonian Parameters of Re(CO)$_3$(P$_3$)$_2$· in Frozen Benzene at 77 K

	axis[a]	g	$A_{Re}/g\beta$,[b] G	$A_P/g\beta$, G
major species	$\parallel$	1.9782	412	14.2
	$\perp$	2.1257	78.7	14.2
minor species	$\parallel$	1.9784	310	

[a] Axial symmetry has been assumed pending further refinement. [b] 1 G = 10^{-4} T.

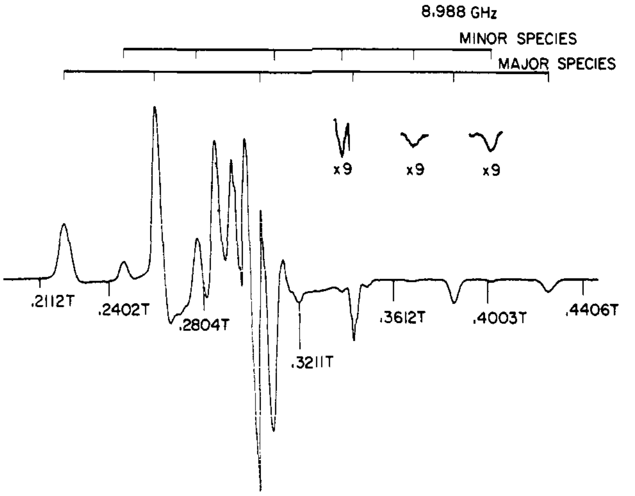

Figure 1. EPR spectrum of a frozen benzene solution (77 K) of Re(CO)$_3$(P-c-Hx$_3$)$_2$·. Parallel-field transitions for both major and minor species are indicated.

We have previously described the formation and properties of Mn(CO)$_3$L$_2$· (L = phosphorus donor ligand) radicals[10] and have studied the hydrogen atom transfer[11] and ligand substitution reactions.[12] Formation of Re(CO)$_3$(P-c-Hx$_3$)$_2$· is accomplished in a manner similar to that described for the manganese radicals. A benzene solution of Re$_2$(CO)$_8$(P-c-Hx$_3$)$_2$ (2.7 mM) and P-c-Hx$_3$ (9.5 mM) in a quartz photolysis tube is irradiated with unfiltered light form a GE sunlamp for 5 h. The solution is occasionally degassed by brief evacuation of the flask. Over the course of the photolysis, the initially colorless solution turns deep blue. A single new infrared absorption in the carbonyl region grows in at 1849 cm^{-1}. Upon exposure to air, the solution immediately loses its blue color and the IR band at 1849 cm^{-1} disappears. No new carbonyl peaks are observed. When CCl$_4$ is added to the solution, the blue color is lost, the IR band at 1849 cm^{-1} disappears, and new peaks appear at 1922 and 1873 cm^{-1}. These peaks are assigned to Re(CO)$_3$(P-c-Hx$_3$)$_2$Cl in analogy with Re(CO)$_3$(PPh$_3$)$_2$Cl[13] which shows absorptions at 1930 and 1880 cm^{-1} with a weak peak at 2036 cm^{-1}.

The frozen solution 9-GHz EPR spectrum has been obtained at 77 K (Figure 1). The spin-Hamiltonian parameters obtained from a computer simulation[14] (prelim-

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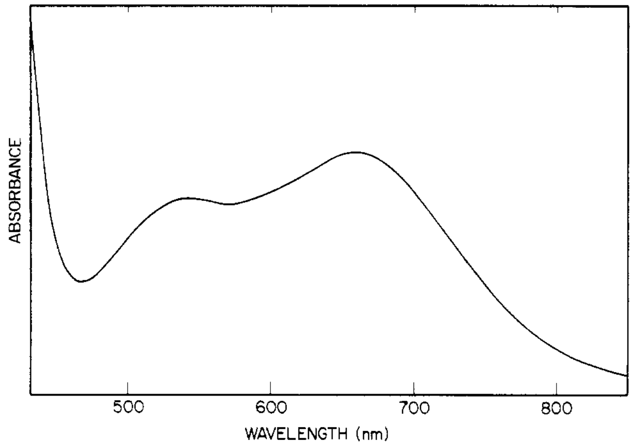

Figure 2. Electronic spectrum of $Re(CO)_3(P\text{-}c\text{-}Hx_3)_2\cdot$ in benzene. (ϵ_{max} ~5×10^2 M^{-1} cm^{-1}).

inary, but quite accurate in reproducing the parallel region) are summarized in Table I. There are two distinct rhenium species present, one in considerably higher concentration than the other. Each shows coupling to Re, which has two isotopes,[15] ^{185}Re (37.05%) and ^{187}Re (62.93%), for which $I = {}^5/_2$. The magnetic moments differ by only 1% so the different isotopes do not account for the two observed species.

If the second species were an impurity, we would expect its relative concentration to vary with the preparation or with change in sample handling. No such variation was observed. In attempts to obtain clear ^{31}P coupling information, we obtained EPR spectra at 4 K both by CW and electron spin echo techniques and also ran CW spectra at 77 K at 3.4 GHz without any improvements in resolution. Fortunately, the phosphorus superhyperfine structure is evident in the fourth parallel Re hyperfine line of the major species, showing the 1:2:1 triplet expected from two essentially equivalent ^{31}P centers. Under increased gain, the corresponding line of the minor species has the same characteristics (see Figure 1). Finally, it should be noted that the EPR parameters of both species are analogous to those for $Mn(CO)_3L_2\cdot$ radicals.[10,16]

The major species is assigned a square-pyramidal structure, with phosphine ligands in basal positions, most probably in a trans disposition. A trans ligand arrangement should cause the spectrum to deviate from axial symmetry, but such deviation cannot be detected without extensive refinement, in progress. The contribution of the minor species to the spectrum is apparently constant from one preparation to another. It is most likely an isomer of the major species; it might correspond to a cis configuration of the phosphines in a distorted square-pyramidal structure.

The room-temperature solution mixture was reacted with excess $HSn(n\text{-}C_4H_9)_3$, to form the rhenium hydride $HRe(CO)_3L_2$. The ^1H NMR spectrum (benzene-d_6) revealed one apparent triplet ($J(^1H\text{-}^{31}P) = 20$ Hz) centered at δ −6.23. This result suggests that if there are two isomers of $Re(CO)_3L_2\cdot$, they interconvert rapidly at room temperature and that one (presumably the trans basal form) reacts more rapidly with the hydrogen atom source.

The UV–visible spectrum in benzene (Figure 2) consists of two broad absorptions at 540 and 665 nm (ϵ ~5×10^2 M^{-1} cm^{-1}). The electronic spectra of the $Mn(CO)_3L_2\cdot$ radicals have been discussed[11] in terms of simple one-electron d–d transitions. While $Mn(CO)_5\cdot$ shows a single absorption band,[17] the effect of phosphine substitution is to split the degeneracy of the d orbitals and shift one transition to longer wavelength. $Re(CO)_5\cdot$ shows a single electronic absorption band at 535 nm.[18] Thus, the change in the electronic spectrum upon substitution of $Re(CO)_5\cdot$ parallels that seen for $Mn(CO)_5\cdot$, except that the transitions are shifted to higher energy as expected for the third-row metal.

We have recently reported kinetics studies of the reaction of CO with $Mn(CO)_3L_2\cdot$ radicals.[12] These studies suggest an associative pathway for ligand substitution by CO. The rate of substitution showed a marked decrease for the bulkiest ligands. Although $P\text{-}c\text{-}Hx_3$ is much bulkier (cone angle = 170°)[9] than $P(i\text{-}Bu)_3$ (cone angle = 142°), preliminary experiments indicate that the rate of reaction of CO with $Re(CO)_3(P\text{-}c\text{-}Hx_3)_2\cdot$ is at least 200 times faster than with $Mn(CO)_3[P(i\text{-}Bu)_3]_2\cdot$. The higher rate for the associative process at rhenium is presumably due to larger size as compared with manganese.

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Registry No. $Re(CO)_3(P\text{-}c\text{-}Hx_3)_2$, 85565-69-1; $Re_2(CO)_8(P\text{-}c\text{-}Hx_3)_2$, 65531-96-6.

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Addition of Alkynyllithium Reagents to the S–S Bond of (μ-Dithio)bis(tricarbonyliron): Equilibria between Open S-Centered and Bridged C-Centered Anions

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Summary: Alkynyllithium reagents cleave the S–S bond of $(\mu\text{-}S_2)Fe_2(CO)_6$ to give $(\mu\text{-}RC{\equiv}CS)(\mu\text{-}LiS)Fe_2(CO)_6$ complexes which apparently are in equilibrium with products of intramolecular S^- addition to the α and/or β carbon atom of the $RC{\equiv}C$ group. With alkyl halides and acetyl chloride S-alkylation or S-acylation was observed. Protonation and reactions with group 4 organometallic halides gave "closed" products, while reaction with methylmercuric chloride gave both "open" and "closed" products.

We have reported that the S–S bond of (μ-dithio)bis(tricarbonyliron) undergoes nucleophilic cleavage by or-

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