discussions and Marshall Welch for synthetic assistance.

Supplementary Material Available: Table S1 giving positional and thermal parameters (3 pages). Ordering information is given on any current masthead page.

Thermal Synthesis and Structural Characterization of $Re(CO)_3(PCy_3)_2$, a Rhenium(0) Radical

Lisa S. Crocker and D. Michael Heinekey*

Department of Chemistry, Yale University
Sterling Chemistry Laboratory, P.O. Box 6666
New Haven, Connecticut 06511-8118

Gayle K. Schulte

Instrument Center, Yale University
Sterling Chemistry Laboratory, P.O. Box 6666
New Haven, Connecticut 06511-8118

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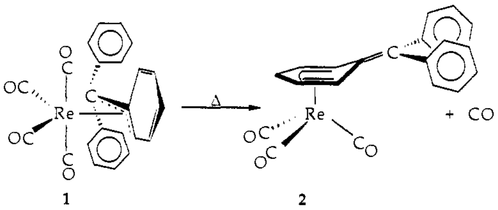
There is considerable interest in radicals of the general type $M(CO)_{5-n}(L)_n$ (M = Mn, Re; L = phosphorus donor ligand) particularly with regard to their structure and reactivity. While the reactivity of these species has been extensively studied, structural data for this class of radicals is limited to inferences from spectroscopic observations. Consistent with theoretical predictions,[1] a C_{4v} square-pyramidal structure for the parent $M(CO)_5$ radicals (M = Mn,[2] Re[3]) has been assigned based on matrix isolation IR studies. In contrast to the facile dimerization of the parent radicals, persistent radicals have been prepared by replacement of two carbonyl groups with bulky phosphine ligands to give the species $M(CO)_3(PR_3)_2$ (M = Mn,[4] Re;[5] PR_3 = bulky phosphine). Such persistent radicals have been well charcterized in solution but have so far not been isolated, presumably due to limitations of the photochemical syntheses employed. We now report an efficient thermal method for the preparation of Re(0) radicals of the type $Re(CO)_3(PR_3)_2$ (PR_3 = bulky phosphine).

We have previously reported the synthesis and properties of $(\eta^3\text{-}CPh_3)Re(CO)_4$ (**1**). Compound **1** reacts with CO to cleanly generate $Re(CO)_5$ radical and triphenylmethyl radical, presumably via the highly unstable σ-bonded intermediate $(CO)_5Re\text{-}CPh_3$.[6] Unfortunately, reaction of **1** with phosphines is limited to those with cone angles[7] less than that of PPh_3 and leads only to diamagnetic products.[8] A more suitable precursor for generating stable radicals can be prepared by thermal decarbonylation of **1** to give $(\eta^5\text{-}CPh_3)Re(CO)_3$ (**2**), which has been fully characterized (eq 1).[9]



(1)

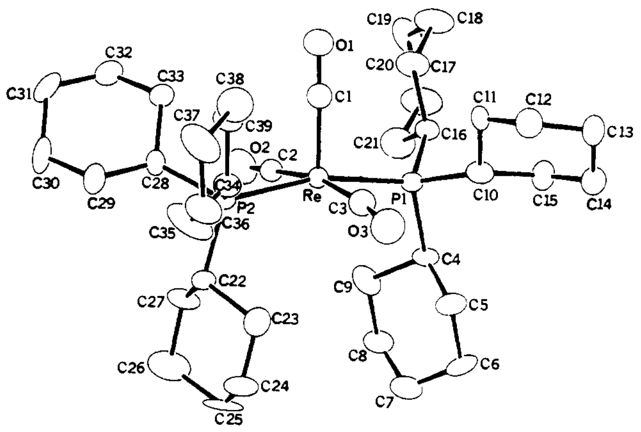


Figure 1. ORTEP projection and labeling scheme for **3**. Atoms are depicted as 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

Compound **2** reacts with excess PCy_3 or $P(i\text{-}Pr)_3$ (benzene, room temperature) to give deep blue solutions of the $Re(CO)_3L_2$ radicals (L = PCy_3, **3**; $P(i\text{-}Pr)_3$,**4**). In each case the presence of radicals was detectable by EPR spectroscopy; the spectra obtained for both complexes were identical with that reported earlier for $Re(CO)_3(PCy_3)_2$.[5] Well formed deep blue needles of **3** suitable for X-ray study precipitated from solution upon standing for several days.[10] The structure of **3** is a distorted square pyramid with $CO_{apical}\text{-}M\text{-}L_{basal}$ angles of 95–98° (see Figure 1).[11] Relevant bond angles are C(1)-Re-P(1) = 97.0 (4)°, C(1)-Re-P(2) = 97.3 (4)°, C(1)-Re-C(2) = 95.1 (6)°, C(1)-Re-C(3) = 98.1 (6)°.

Spetroscopic data for **3** are also consistent with the square-pyramidal structure. The infrared spectrum of **3** exhibits one band in the CO stretching region (ν_{CO}(benzene) 1849 (s) cm^{-1}).[12] The electronic spectrum (benzene solution) shows three bands (λ_{max}

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(8) The results of experiments involving reaction of **1** with a variety of phosphines will be reported separately.

(9) A THF solution (4 mL) of **1** (380 mg, 0.702 mmol) was degassed in a tube equipped with a high-vacuum Teflon stopcock and heated in a 90 °C oil bath for 24 h. The product, upon recrystallization from heptane, was isolated in 78% yield (280 mg). Anal. Calcd for $C_{22}H_{15}O_3Re$: C, 51.36; H, 2.92. Found: C, 51.28; H, 3.07. IR (heptane) ν(CO): 2033 (m), 1956 (s), 1944 (s) cm^{-1}. ^1H NMR (acetone-d_6, 298 K, 250 MHz) δ 7.35–7.27 (m, 4 H, free ortho), 7.16–7.06 (m, 6 H, free meta, para) 5.98 (tt, J = 6, 1 Hz, 1 H, coord. para), 5.70 (m, 2 H, coord. meta), 4.89 (dd, J = 8, 1 Hz, 2 H, coord. ortho). An X-ray study of **2** confirmed the structure suggested by the spectroscopic data.

(10) The magnetic susceptibility, measured using the method of Evans (Evans, D. F. *J. Chem. Soc.* **1959**, 2003–2005), corresponds to one unpaired electron.

(11) Summary of X-ray analysis: The structure of **3** was determined by X-ray crystallography using a crystal that measured 0.50 × 0.25 × 0.13 mm. The crystal was mounted in a sealed capillary in a glovebox and care was taken to ensure that the sample did not come into contact with air. Data collection was done at −75 °C. Diffraction measurements were made on a Rigaku AFC5S fully automated diffractometer using graphite monochromated Cu Kα radiation (λ = 1.54178 Å). Preliminary indications of the unit cell based on 25 randomly selected reflections revealed monoclinic symmetry. The data were processed with the high angle cell with the following lattice parameters: a = 10.011 (2) Å, b = 20.277 (4) Å, c = 21.094 (2) Å, β = 92.923 (9)°. The space group, based on the systematic absences: $0k0$, $k = 2n + 1$; $h01$, $h + 1 = 2n + 1$ was uniquely assigned as $P2_1/n$ with one molecule of composition $C_{39}H_{66}ReO_3P_2$ and one molecule of the solvent of crystallization, benzene, forming the asymmetric unit. The volume was 4276 (1) Å^3 and the calculated density was 1.41 g/cm^3. There were 6786 unique reflections collected with $2\theta \leq 120°$, of those reflections 3894 (57%) with $I \geq 3\sigma(I)$ were adjudged observed. The data were corrected for Lorentz factor, polarization, and absorption using DIFABS. Correction for absorption by the psi scan method was also tried but the R factor was less satisfactory (R = 0.074 and R_w = 0.089). The structure was solved by locating the position of the rhenium atom using the Patterson function. Iterative use of the WFOURIER option in DIRDIF revealed the entire non-hydrogen structure. The hydrogens were input at their calculated locations. The full-matrix refinement of the non-hydrogen atoms, with the exception of the carbonyl carbons which remained isotropic (the carbonyl carbons C1, C2, and C3 go non-positive definite upon anisotropic refinement), and input of the hydrogen scattering factors resulted in convergence of the crystallographic reliability factor to an unweighted residual of 0.053 and a weighted residual of 0.065. All intramolecular bond distances and angles are within normal ranges.

(12) Previously reported IR spectral data for **3**:[5] ν_{CO}(benzene) 1849 cm^{-1}.

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661 nm, ϵ = 365 M^{-1} cm^{-1}; λ_{max} 518 nm, ϵ = 290 M^{-1} cm^{-1}; λ_{max} 415 nm, ϵ = 835 M^{-1} cm^{-1}).[13]

It is of interest to compare the structure of **3** with the analogous W(0) complex $W(CO)_3(PCy_3)_2$ (**5**) reported by Kubas and coworkers.[14] Compound **5** is a 16-electron d^6 species that exhibits an agostic interaction between the tungsten center and one of the β C–H bonds of one cyclohexyl ring. We find no evidence for such an interaction in **3**, although the structures are otherwise quite similar.[15] This is understandable since the HOMO of **3** (a_1 in C_{4v}, predominantly d_{z^2} in character) is singly occupied, and such an interaction would lead to a 19-electron complex.

Preliminary studies of the reactivity of **3** have confirmed the previously reported observations[5] that **3** reacts rapidly with CO to give $(PCy_3)_2Re_2(CO)_8$ (eq 2) and with tin hydrides to afford the neutral hydride $(PCy_3)_2Re(CO)_3H$ (**6**) (eq 3). In contrast to **5**, **3** reacts very slowly with H_2 (25 psi, benzene, 25 °C, 8 weeks).[16] The fact that this reaction proceeds so slowly is surprising since the related d^7 species $Co(CN)_5^{3-}$ [17] and other transition-metal radicals[18] react rapidly with H_2 via so-called "homolytic" cleavage to afford metal hydrides. In the case of $Co(CN)_5^{3-}$, the results of kinetic studies are consistent with a termolecular reaction, requiring two cobalt centers in relatively close proximity.[19] The extremely bulky PCy_3 ligands (cone angle of 170°)[7] may impose a large steric barrier to such a reaction of **3** with H_2. For the related radical **4**, substituted with smaller $P(i\text{-}Pr)_3$ groups (cone angle of 160°),[7] the reaction with H_2 (25 psi, 25 °C) is complete within 3 days.

$$2Re(CO)_3(PCy_3)_2 + 2CO \rightarrow Re_2(CO)_8(PCy_3)_2 \qquad (2)$$

$$2Re(CO)_3(PCy_3)_2 + 2Ph_3SnH \rightarrow \underset{\mathbf{6}}{2Re(CO)_3(PCy_3)_2H} + Ph_3Sn\text{-}SnPh_3 \qquad (3)$$

The synthetic methodology employed here is potentially general. In particular, the clean synthesis of radicals that are themselves photolabile is possible. We are continuing to investigate the synthesis and reactivity of radicals generated thermally from **2** and related precursors.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this research. The receipt of a Cottrell Grant from the Research Corporation is gratefully acknowledged. L.S.C. is grateful for a Connecticut High Technology Graduate Scholarship.

Supplementary Material Available: Complete X-ray analysis of **3**, including summary of data collection and processing parameters, tables of positional and thermal parameters, and bond distances and angles (8 pages); tables of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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(13) Previously reported UV–vis spectral data for **3**:[5] 540 nm, 665 nm ϵ ~ 5 × 10^2 M^{-1} cm^{-1}.

(14) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294–2301.

(15) The shortest Re–C bond distance to a cyclohexyl ring carbon in **3** is 3.7 Å.

(16) 250-MHz ^1H NMR (benzene-d_6) for **6**: t, −6.23 ppm, J_{PH} = 20 Hz.

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(19) Halpern, J. *Inorg. Chim. Acta* **1983**, *77*, L105.

Novel Electron-Transfer Photocyclization Reactions of α-Silyl Amine α,β-Unsaturated Ketone and Ester Systems

Wei Xu,[1] Yoon T. Jeon,[1] Eietsu Hasegawa,[1] Ung C. Yoon,[2] and Patrick S. Mariano*,[1]

Department of Chemistry and Biochemistry
University of Maryland, College Park, Maryland 20742
Pusan National University, Pusan 609-735, Korea

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Our studies in the area of electron transfer (SET) photochemistry have recently focused on photoaddition reactions between α-silyl amines and conjugated cyclohexenones.[3] Results from earlier efforts which demonstrate that (1) SET pathways are followed in excited state reactions between tertiary amines and cyclohexenones[4] and (2) photoinduced SET-desilylation sequences serve as selective methods for carbon-radical generation[5] have served to guide these initial studies. We have shown[3] that the tertiary silyl amine **3** photoadds to cyclohexenones **2** to yield adducts **1** and **4** in ratios that are dependent upon the reaction conditions used. In media that favor reaction via contact ion radical pairs (CIRP), TMS-adducts **4** are formed preferentially through sequential SET–proton transfer routes while non-TMS adducts **1** arising via sequential SET–desilylation paths predominate in media that favor solvent separated radical ion pair (SSIRP) formation (Scheme I). In a parallel study,[5] we noted that 9,10-dicyanoanthracene (DCA) can photosensitize additions of **3** to **2**, giving non-TMS adducts **1** predominantly by a route involving conjugate addition of an α-amino radical to the enones.

Thoughts about the synthetic potential of these processes led to an investigation of preparative and mechanistic aspects of α-silyl aminoalkyl unsaturated ketone and ester photocyclization reactions. We felt that reactions of these systems induced by direct or SET-sensitized irradiation methods could occur via respective anion diradical **5** or radical **6** cyclization modes (Scheme II). Results from this effort, reported below, have demonstrated the mechanistic and synthetic interest of these processes.

Direct irradiation[6] of cyclohexenone derivative **7**[7] in MeOH (N_2) leads to efficient (71%)[6] production of spirocyclic amine **8**. Also, stereoisomeric hydroisoquinolones **10** (40%) and **11** (51%) along with traces of hydroindolone **12** arise from irradiation of **9** under these conditions.[6,7] The product ratio changes in favor of **12** (34% and **10** (27%), **11** (31%)) when air-saturated solutions of **9** are directly irradiated. Photocyclizations of **7** and **9** can be SET sensitized. Thus, irradiation of DCA (8 × 10^{-5} M)[6] in a MeOH solution containing **7** gives **8** (78%) while **10** (71%), **11** (13%), and **12** (2%) are produced from DCA-sensitized reaction

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(1) University of Maryland.

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(6) Irradiation conditions are as follows: uranium-filter ($\lambda > 320$ nm), N_2 atmosphere, [enone] and [ester] = 2 × 10^{-3} M, [DCA] or [DCN] = 4 × 10^{-4} (for sensitized reactions unless otherwise noted). Reactions were monitored by UV and GLC and conducted to >95% conversion. Product separations were by GLC or column (silica gel) chromatography. The reported yields are for isolated substances.

(7) Synthetic and structure and stereochemistry determination methods will be discussed in a full paper.

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