Contribution from The School of Chemical Sciences,
University of Illinois, Urbana, Illinois 61801

Thermal and Photochemical Substitution Reactions of the Tricarbonyl(cyclopentadienyl)hydrido Compounds of Tungsten and Molybdenum[1]

NORRIS W. HOFFMAN and THEODORE L. BROWN*

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The substitution of $HW(CO)_3(\eta^5\text{-}C_5H_5)$ (**1**) by tributylphosphine is found to occur in heptane in the dark at nonreproducible rates, to yield a cis–trans mixture of monosubstituted products. Studies involving other ligands show that the rate of the thermal reaction in the dark varies greatly with ligand, but the poor reproducibility of the thermal reaction rates precludes any detailed analysis of ligand effects. Addition of galvinoxyl, nitrosodurene, or benzoyl peroxide causes marked catalysis of the reaction. Irradiation using 500-nm light of a heptane solution containing small concentrations of either dimer, $M_2(CO)_6(\eta^5\text{-}C_5H_5)_2$, causes very rapid substitution, with quantum yield about 1000 when M = W and greater than 50 when M = Mo. Irradiation of heptane solutions of **1** and PBu_3 at 311 nm causes substitution with $\Phi > 30$, presumably as a result of homolysis of the W–H bond. The molybdenum analogue $HMo(CO)_3(\eta^5\text{-}C_5H_5)$ (**2**) undergoes thermal substitution by PBu_3 at least 10^6 times more rapidly than **1**. On the other hand, reaction of **2** with $AsPh_3$ is slow and not subject to photoinitiation by 500-nm irradiation of $Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2$. The results are accounted for in terms of a chain mechanism involving the intermediacy of $M(CO)_3(\eta^5\text{-}C_5H_5)\cdot$ radicals which undergo rapid substitution.

Introduction

Recent work in these laboratories[2-4] has established the existence of radical chain mechanisms in reactions of metal carbonyls, eq 1 and 2. Because transition-metal hydrides play

$$Cl_3SnCo(CO)_4 + 2L \rightarrow [Co(CO)_3L_2]SnCl_3 \qquad (1)$$
$$L = AsPh_3, PPh_3, PBu_3$$

$$HM(CO)_5 + L \rightarrow HM(CO)_4L + HM(CO)_3L_2 \qquad (2)$$
$$L = PBu_3; M = Mn, Re$$

important roles in many organic reactions promoted by organometallic compounds, we were especially interested in examining other hydride systems in hope of detecting similar radical reactions. The tungsten compound $HW(CO)_3(\eta^5\text{-}C_5H_5)$ (**1**) represented a logical starting point, for it is easily prepared and handled;[5] moreover, its ligand substitution reactions proceed relatively slowly under ambient conditions and lead cleanly to a cis–trans mixture of monosubstituted hydride complexes $HW(CO)_2L(\eta^5\text{-}C_5H_5)$.[6]

In this paper, the following labels are employed. $M(CO)_2L(\eta^5\text{-}C_5H_5)X$: (**1**) M = W, X = H, L = CO; (**2**) M = Mo, X = H, L = CO; (**5**) M = W, X = Cl, L = CO; (**1-L**) M = W, X = H, L = L etc. $M_2(CO)_6(\eta^5\text{-}C_5H_5)_2$: (**3**) M = W; (**4**) M = Mo.

Experimental Section

Materials. The complexes $HW(CO)_3(\eta^5\text{-}C_5H_5)$[5] (**1**), $HMo(CO)_3(\eta^5\text{-}C_5H_5)$[6] (**2**), $W(CO)_3(\eta^5\text{-}C_5H_5)Cl$[7] (**5**), and $[Mo(CO)_3(\eta^5\text{-}C_5H_5)]_2$[8] (**4**) were prepared according to literature procedures. Nitrosodurene was prepared using the method of Smith and Taylor[9] and phenyl-*tert*-butylnitrone via that of Iversen and Lund.[10] Galvinoxyl [2,6-di-*tert*-butyl-α-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadiene-1-ylidine)-*p*-tolyloxy] (Aldrich), trityl chloride (Aldrich), and benzoyl peroxide (MCB) were used as received. Tri-*n*-butylphosphine, PBu_3 (Aldrich), was heated 12 h at 65 °C with $LiAlH_4$ and then distilled at 15 mm; the fraction boiling at 129 °C was collected. Triethyl phosphite, $P(OEt)_3$, and triisopropyl phosphite, $P(O\text{-}i\text{-}Pr)_3$ (Aldrich), were stirred 12 h at 30 °C over sodium and distilled under reduced pressure; fractions distilling at 83 °C (60 mm) and 71 °C (16 mm), respectively, were collected. Triphenylphosphine, PPh_3 (Aldrich), was recrystallized five times from ethanol in an inert-atmosphere chamber. The phosphorus ligands were stored under argon in Schlenk tubes. Triphenylarsine (Aldrich) was recrystallized (without excluding air) from ethanol and hexane and stored under argon. Benzene (B & A reagent) and *n*-heptane (Phillips bulk) were purified by extensive extraction of olefins with concentrated sulfuric acid, neutralization of the solvent phase with aqueous $NaHCO_3$, drying over anhydrous $MgSO_4$, and distillation from sodium benzophenone ketyl under argon. Tetrahydrofuran (THF) was also distilled from the ketyl under argon.

The dimer $[W(CO)_3(\eta^5\text{-}C_5H_5)]_2$ (**3**) was prepared from **5**. To an amalgam of sodium (0.8 g, ~30 mmol) in 5 mL of mercury under 50 mL of THF was added solid **5** (1.358 g, 3.69 mmol). This mixture was stirred 75 min at 30 °C and allowed to stand 30 min. The pale yellow supernatant liquid was transferred into another vessel under argon via syringe tubing. The residual amalgam was washed once with 30 mL of THF; the washing was combined with the initial supernatant. To this solution of $Na[W(CO)_3(\eta^5\text{-}C_5H_5)]$ was added solid **5** (1.352 g, 3.69 mmol). The resulting mixture was heated at reflux for 3 days in the dark to afford upon cooling to 20 °C a blood red solution over red and white solids. Solvent was removed at reduced pressure with exposure to light minimized; the resulting solid material was washed extensively with water to remove NaCl. Yield of **3**, 2.21 g (90%). The IR spectrum of a saturated solution of product in heptane showed bands in the CO stretching region only at 1962 and 1914 cm^{-1} expected for the dimer.[11]

General Procedures. All reactions were carried out using Schlenkware and glass or stainless steel syringe tubing or Hamilton gastight syringes for transferring liquids and suspensions. Argon (Linde) or prepurified nitrogen (Linde) was used without further purification unless explicitly stated. Solution transfers and sample withdrawals were performed under positive gas pressure using carefully purged equipment. Except where irradiation is indicated, exposure to light other than red photographic safelight was rigorously minimized in all experiments.

Kinetics Studies. The reactants were mixed in heptane in a small Schlenk tube fitted with rubber septum at either ambient temperature or 0 °C. For NMR studies the resulting solution (initially 0.026 M in **1**) was rapidly transferred under argon pressure through stainless steel syringe tubing into a purged, septum-capped NMR tube. Spectra were recorded on instruments (Varian HR220 at 28 °C, or Varian EM390 at 35 °C) which employed no devices using visible or UV light for measuring tube spinning rate.

Substitution in heptane solutions was followed by observation of the singlet at $\tau = 5.34$ due to **1** and the slightly broadened singlet at $\tau = 5.56$ due to **1**-PBu_3 or the analogous signal due to substitution by other ligand L. Known quantities of air were introduced into samples when desired using Hamilton gas-tight syringes. Several reactions were also followed in NMR tubes sealed under vacuum; in the latter case, the solution initially under argon was degassed with four freeze–thaw cycles (10^{-4} Torr).

IR Spectra. Spectra were recorded on a Beckman IR-7 or 4240 spectrophotometer; the sample beam was passed through a germanium filter (Optical Coating Laboratory, Inc.) to remove visible and UV light. Either NaCl (1.0, 0.5, or 0.25 mm path length) or "discardable" polyethylene (1.0 mm path length, Barnes Engineering Co.) cells were used. The latter were modified for anaerobic sampling by inserting stainless steel syringe needles (19 gauge) with Luer fittings into the opening at the top of the cell cavity and through the bottom wall of the cavity. The needles were held in place using Loctite (TM) Super Bonder glue. The bottom needle was shaped so that the Luer fitting pointed diagonally up to reduce infusion of air. Acceptable spectra could be obtained with the polyethylene cells only at high gain, because polyethylene absorbs strongly in the regions 2060–2000 and 1915–1860 cm^{-1}. The absorbances at 2026 cm^{-1} due to **1** and in the 1966–1954 cm^{-1} range due to **1**-PBu_3 were measured as integrated absorbances to minimize errors associated with the background absorptions due to the cells.

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Table I. Characteristics of Filters Used in Photochemical Experiments

λ_{max}, nm	Type[a]	Bandwidth at half-height, nm	Transmittance at λ_{max}, %
500	I	12	57
444	I	15	58
400	I	13	30
400	B	75	67
358	B	78	61
350	I	15	15
311	I	8	2
254	I	20	16

[a] Key: I = interference, B = glass absorption.

For kinetics experiments, a solution of known concentration of **1** was prepared. Its IR spectrum was then recorded to determine initial absorbance and to ensure the absence of dimer. A known amount of PBu_3 was added, the resulting solution was stirred briefly and then transferred into a water-jacketed reaction vessel maintained at 33–34 °C. Samples were withdrawn periodically and analyzed as described above. Alternately, in-cell monitoring of reaction progress was carried out by repeated scanning over the range 2060–1800 cm^{-1}, with the same sample tightly sealed in a NaCl cell.

The substitution of $HMo(CO)_3(\eta^5\text{-}C_5H_5)$ (**2**) was studied using a simple stopped-flow instrument described elsewhere.[4] Reaction of **2**, 2.4×10^{-3} M, with PBu_3, 2.4×10^{-2} M, in heptane was studied at 30 °C. Following mixing, the absorption at 2029 cm^{-1} due to **2** was observed to decline to zero in less than 10 s. Essentially identical results were obtained for seven successive mixings.

Electronic Spectra. Solutions (approximately 10^{-4} M) were prepared under argon and transferred via syringe tubing into septum-capped cells (1 cm path length) which had been well purged with argon. Spectra were obtained using a Cary Model 14 spectrophotometer.

Photochemical Experiments. Except where otherwise indicated, photochemical studies were conducted using a high-pressure 1000-W xenon arc lamp (PEKB1000) with Schoeffel housing and collimator fitted with 5-cm path length water filter to remove IR radiation. Selected wavelength ranges were obtained using filters (Oriel or Corion) whose characteristics are listed in Table I. Jacketed photocells of 7.0 cm path length with Pyrex optical flat windows were employed for photoreactions unless otherwise stated. Quantum yield calculations were based on standard ferrioxalate actinometry.[12] The actinometric measurements were performed both before and following irradiations of sample solutions, without any alterations in light source.

Results

Substitution of $HW(CO)_3(\eta^5\text{-}C_5H_5)$ by PBu_3. The thermal substitution of **1** proceeds smoothly in heptane to form the monosubstituted compound, **1**-PBu_3. The IR spectrum of the reaction solution shows appearance of new bands at 1935, 1866, and 1954 cm^{-1}. The latter two absorptions always appear in the same ratio of intensities. It appears that a cis–trans mixture of the monosubstituted products, interconverting rapidly on the time scale of the kinetics experiments, is formed. There is substantial evidence from NMR studies for a facile interconversion of cis–trans isomers in this type of compound.[13]

The kinetics studies were carried out using either NMR or IR to follow the reaction, under conditions of excess substituting ligand. In general, the observed kinetics did not conform to a simple rate law. Assuming a pseudo-first-order rate law, the NMR data yielded linear plots for about 2 half-lives but then showed marked departures from linearity in the direction of increased reaction rate. The second-order rate constants calculated from the limited linear portions of the graphs varied from 2 to 8×10^{-3} M^{-1} s^{-1}. It was found that the presence of added O_2 did not significantly affect the results.

The kinetics studies carried out using IR to follow the reaction yielded similar results. However, the nonlinearity in pseudo-first-order rate law graphs occurred early in the reaction. The concentrations of reactants were about an order of magnitude lower in the IR as compared with the NMR studies. Crude estimates of second-order rate constants yielded much lower values than obtained from the NMR studies, and reproducibility was poor. Again, it was found that the presence of O_2 had no marked effect on reaction rate. Furthermore, addition of O_2 did not result in formation of a detectable amount of dimer.

A large catalytic effect was noted when cells of NaCl window materials were employed in the IR studies. For solutions allowed to remain in the IR cell, the reaction proceeded at least an order of magnitude more rapidly than for solutions under otherwise similar conditions in glass vessels. In addition, reactions proceeding in the IR cells were often observed to suddenly undergo abrupt changes in rate. These catalytic effects were avoided by use of modified polyethylene cells, as described in the Experimental Section.

Effect of Added Reagents. The thermal reaction of **1** with PBu_3 in heptane in the dark is quite slow at 25 °C. For example, a 2×10^{-3} M solution of **1** with 2×10^{-2} M PBu_3 exhibited less than 1% conversion to **1**-PBu_3 after 17 h, as determined by IR analysis. However, addition of galvinoxyl[14] or the spin trap nitrosodurene in quantities of less than 20 mol % relative to **1** effected complete conversion of **1** to **1**-PBu_3 in the dark in less than 15 min, with no dimer formation. An increase in rate of at least 4×10^3 for galvinoxyl or nitrosodurene can be estimated from the observation that a reaction under comparable conditions in the absence of such added reagents was only 25% complete after 240 h.

On the other hand, the presence of a nearly stoichiometric amount of the spin trap phenyl-*tert*-butylnitrone (PBN) increased the rate of 25 °C only by a factor of about 14. A similar phenomenon of slightly greater magnitude was observed with added benzoyl peroxide (BZP) at 55 °C. Increasing rates were noted with increasing amounts of added BZP to an increased rate of about 200-fold upon addition of 33 mol % BZP relative to **1**. No formation of **3** was observed in substitution reactions promoted by PBN or BZP.

At ambient temperature in heptane **1** reacts with 1 equiv of galvinoxyl in the absence of PBu_3 to generate the dimer **3**, as indicated by appearance of IR bands at 1962 and 1914 cm^{-1} and formation of a dark red crystalline precipitate. Addition of nitrosodurene in 0.4 molar ratio to **1** under similar conditions resulted in slow decomposition of **1** to **3** and formation of heptane-insoluble products; ratios of spin trap to **1** larger than unity produced mainly decomposition to unknown products and formation of only trace amounts of dimer. In contrast, the IR spectra of solutions containing stoichiometric mixtures of **1** and PBN at 25 °C or BZP at 55 °C, stirred 5 h, remained unchanged.

Initiation of Ligand Substitution in $HW(CO)_3(\eta^5\text{-}C_5H_5)$ by Photolysis of Metal Dimers. Irradiation of a standard reaction mixture of **1** and PBu_3 in heptane at 25 °C with 500-nm light had no effect on the substitution reaction rate. After 1 h no decrease in concentration of **1** or increase in concentration of **1**-PBu could be detected using IR. Analogous irradiation of reaction mixtures to which small amounts (<10 mol %) of either of the dimers **3** or **4** had been added resulted in extremely rapid substitution. In an experiment employing 9 mol % **3** as photoinitiator, a lower limit of the quantum yield (i.e., the number of molecules of **1**-PBu_3 produced for every photon entering the reaction mixture) was determined to be 1.0×10^3. Although the quantum yield was not accurately measured for the analogous catalysis by **4**, a lower limit of 50 can be conservatively estimated.

The photoreaction at 500 nm between the metal hydrides and the dimers, eq 3, was also investigated. Irradiation using

$$2HM(CO)_3(\eta^5\text{-}C_5H_5) + M'_2(CO)_6(\eta^5\text{-}C_5H_5)_2 \rightleftarrows 2HM'(CO)_3(\eta^5\text{-}C_5H_5) + M_2(CO)_6(\eta^5\text{-}C_5H_5)_2 \quad (3)$$

500-nm light for 15 min of a mixture (2:1 molar ratio) of **2**

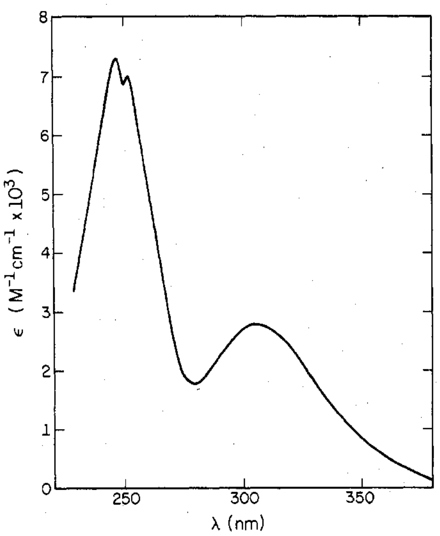

Figure 1. Electronic spectrum of $HW(CO)_3(\eta^5\text{-}C_5H_5)$ in heptane solution, 2×10^{-4} M.

and **3** in heptane at 25 °C (**3** is only slightly soluble in heptane) resulted in formation of an IR band at 1919 cm^{-1}, consistent with formation of **4**. On the other hand, 500-nm irradiation of a mixture (2:1 molar ratio) of **1** and **4** in heptane at 25 °C for 180 min did not generate an IR band at 1914 cm^{-1} expected if **3** were being formed. (Other IR bands for the two hydrides and dimers could not be distinguished due to the proximity in frequencies of the molybdenum and tungsten analogues.) Similar irradiation for 45 min of a more concentrated mixture of **2** and **3** in benzene (no reaction was observed in the dark at 25 °C in 120 min) effected slow conversion of the reactants into **1** and **4**. The initial ^1H NMR singlets at (relative to C_6H_6) −2.57 ppm ($\eta^5\text{-}C_5H_5$ protons of **2**) and −12.65 ppm (H–Mo) had decreased slightly in intensity; new signals at −2.42 ppm (singlet, $\eta^5\text{-}C_5H_5$ protons of **4**), −2.62 ppm (singlet, $\eta^5\text{-}C_5H_5$ protons of **1**), and −14.37 ppm (singlet with ^{183}W satellites due to H–W) had appeared in intensities relative to those of **2** to indicate about 10% interconversion of the respective hydrides and dimers. Further irradiation for 4 h increased the ratio of **1** to **2** to 0.5. No decrease in intensity of the $\eta^5\text{-}C_5H_5$ resonance due to **3** at −2.44 ppm was observed, due to the limited solubility of **3** in benzene. No signals for the $\eta^5\text{-}C_5H_5$ protons of the bimetallic dimer $(\eta^5\text{-}C_5H_5)(CO)_3W\text{–}Mo(CO)_3(\eta^5\text{-}C_5H_5)$ expected to be produced in such a photolytic reaction were seen; however, the small difference in chemical shifts between the ring protons of **4** and **3** (−2.42 and −2.44 ppm) and the somewhat broadened nature of these signals do not allow the conclusion that no mixed dimer was generated. Prolonged 500-nm irradiation of a mixture of **1** and **4** (2:1 mole ratio in benzene) did not result in appearance of the hydride resonance at −12.65 ppm characteristic of **2**.

Photochemical Substitution of PBu_3 into $HW(CO)_3(\eta^5\text{-}C_5H_5)$. A heptane solution of the pale yellow complex **1** exhibits three maxima in its electronic spectrum: 305 nm (ϵ 2.7×10^3 M^{-1} cm^{-1}), 253 nm (ϵ 7×10^3 M^{-1} cm^{-1}), and 248 nm (ϵ 7×10^3 M^{-1} cm^{-1}) (Figure 1). The low-energy band tails extensively into the visible region; ϵ at 400 nm is 40 M^{-1} cm^{-1}. Irradiation of a 0.002 M heptane solution of **1** with light of >400 nm produced no change in IR spectrum; however, light of wavelength <400 nm promoted slow decomposition into **3**. Exposure of a heptane solution of **1** and a fivefold excess of trityl chloride, Ph_3CCl, to sunlamp radiation, using the 358 nm filter, at 30 °C for 95 min effected complete transformation of the hydride into **5**, eq 4. The same mixture had been stirred prior to photolysis for 21 h at 30 °C in the dark with no detectable reaction. Irradiation of solutions (1:10) of **1** and PBu_3 in heptane at 25 °C with 444 nm or longer wavelength light caused no increase in the rate of ligand substitution. Shorter wavelength light (<400 nm) did, however, promote conversion of **1** to **1**-PBu_3 with no formation of **3**. When a solution 9×10^{-4} M in **1** and 9×10^{-3} M in PBu_3 was irradiated with 311-nm light of low intensity, quantum yields dependent upon duration of light exposure were measured. One portion of the solution irradiated for 20 min showed $\Phi = 6$ (5% completion), whereas another aliquot, irradiated for 87 min, afforded $\Phi > 30$. Likewise, an experiment using a different solution of **1** and PBu_3 yielded $\Phi = 16$ for 19 min of exposure.

$$HW(CO)_3(\eta^5\text{-}C_5H_5) + CPh_3Cl \xrightarrow[h\nu\ (295\text{–}410\ \text{nm})]{n\text{-heptane, }30\ ^\circ C} W(CO)_3(\eta^5\text{-}C_5H_5)Cl \qquad (4)$$

Reactions of $HW(CO)_3(\eta^5\text{-}C_5H_5)$ with Ligands of Varying Nucleophilic Strength. Reaction rates of **1** at 35 °C in benzene with tenfold excesses of ligands $AsPh_3$, PPh_3, $P(O\text{-}i\text{-}Pr)_3$, and PBu_3 were followed using ^1H NMR. In contrast to those measured in heptane, the chemical shifts of the $\eta^5\text{-}C_5H_5$ proton singlets of the product hydrides **1**-L are lower than that of **1** (measured in parts per million upfield of benzene): L = PBu_3, 2.29; PPh_3, 2.40; $P(O\text{-}i\text{-}Pr)_3$, 2.19. No formation of product was observed after 4 h in the dark for L = $AsPh_3$ or PPh_3. Exposure of the reaction mixture containing $AsPh_3$ to fluorescent light for 25 min produced no change in NMR spectrum, whereas a spectrum of the PPh_3-containing solution after 20 min of irradiation showed one-third conversion of **1** to **1**-PPh_3. Further irradiation of the mixture effected no further substitution. Between addition of PBu_3 to the solution of **1** and the recording of the first spectrum (25 min at 25–35 °C), the reaction was approximately 20% complete. Over the next 15 min at 35 °C, substitution proceeded to 35% conversion. Exposure for 2 min of the tube to fluorescent light afforded an increase in reaction rate, leading to almost total conversion of **1** into **1**-PBu_3. Reaction of **1** with $P(O\text{-}i\text{-}Pr)_3$ was faster than with the other ligands. The first spectrum recorded 18 min after addition of $P(O\text{-}i\text{-}Pr)_3$ to **1** (25–35 °C) showed 60% conversion of **1** into **1**-$P(O\text{-}i\text{-}Pr)_3$. Substitution proceeded to completion at 35 °C in another 45 min.

Ligand Substitution Reactions of $HMo(CO)_3(\eta^5\text{-}C_5H_5)$. The molybdenum hydride reacts much more rapidly with nucleophiles than its tungsten analogue. A stopped-flow study employing heptane solutions 0.0024 M in **2** and 0.024 M in PBu_3 showed complete conversion of **2** into **2**-PBu_3 in less than 10 s at 30 °C. Similarly, the IR spectrum indicated total transformation of **2** into **2**-$P(OEt)_3$ by a tenfold excess of $P(OEt)_3$ at 30 °C in hexane within 15 min. By contrast, however, no conversion of **2** into **2**-$AsPh_3$ or **4** was observed at 25 °C for a heptane solution 1.3×10^{-3} M in **2** and 1.3×10^{-2} M in $AsPh_3$, after 15 h. Addition of a small quantity of **4** to the solution followed by 35 min of irradiation with 500-nm light produced no **2**-$AsPh_3$.

Discussion

The thermal substitution reactions of **1** and **2** with phosphorus ligands were first studied by Green and co-workers.[6] They reported a second-order rate constant for reaction of **1** with PPh_3 in benzene at 65 °C and measured an essentially identical rate constant for reaction of the tungsten deuteride. Although experimental details are sparse, the authors indicated that reaction solutions were sealed in ampules and that reaction progress was monitored by IR, using cells with NaCl windows. The extent to which solutions were protected from exposure to light and air was not indicated.

We have not been able to obtain reproducible kinetics results that fit the rate law for a second-order reaction. However, the rates of reaction which we do observe from the IR spectra would correspond roughly to second-order rate constants at

34 °C in the range from 10^{-4} to 10^{-3} M^{-1} s^{-1}. Thus, the rates we observe for the reactions at 34 °C in heptane are comparable to those observed by Green and co-workers at 65 °C in benzene. The results we obtain from NMR studies of benzene solutions also suggest much greater rates at 35 °C than would be expected from the earlier report.

The poor reproducibility of our kinetics studies suggests the operation of a radical chain pathway for substitution. The marked catalytic effects of NaCl cell windows, also observed in other systems where a radical chain mechanism seems to be operative,[3,15] and the very large catalytic effect of added reagents such as galvinoxyl or nitrosodurene strongly support the idea that there is an accessible radical chain pathway. On the other hand, traces of O_2 do not seem to affect reaction rates very much, whereas substantial effects were noted in other related systems.[2,4]

A radical chain pathway for substitution, in analogy with that proposed for substitution of $HRe(CO)_5$, is outlined in eq 5 through 10.

$$R\cdot + HM(CO)_3(C_5H_5) \rightarrow RH + M(CO)_3(C_5H_5)\cdot \tag{5}$$

$$M(CO)_3(C_5H_5)\cdot \rightleftarrows M(CO)_2(C_5H_5)\cdot + CO \tag{6}$$

$$M(CO)_2(C_5H_5)\cdot + L \rightleftarrows M(CO)_2L(C_5H_5)\cdot \tag{7}$$

$$M(CO)_2L(C_5H_5)\cdot + HM(CO)_3(C_5H_5) \rightarrow HM(CO)_2L(C_5H_5) + M(CO)_3(C_5H_5)\cdot \tag{8}$$

$$R\cdot + M(CO)_{3-n}L_n(C_5H_5)\cdot \rightarrow RM(CO)_{3-n}L_n(C_5H_5) \tag{9}$$

$$M(CO)_{3-n}L_n(C_5H_5)\cdot + M(CO)_{3-m}L_m(C_5H_5)\cdot \rightarrow M_2(CO)_{6-m-n}L_{m+n}(C_5H_5)_2 \qquad n, m = 0 \text{ or } 1 \tag{10}$$

The initiating radicals R· may be present adventitiously; this is presumably the case in those solution mixtures prepared for kinetics analysis. The variable rates observed can be ascribed to varying small concentrations of radical species in solution or on the walls of the glass vessels. The increases in rates observed when the solutions are placed in IR cells with NaCl windows are ascribed to sites on the salt plate surfaces that either function as radicals or provide a site for radical generation. Similar catalytic effects of IR cell windows have been observed in other metal carbonyl reactions thought to proceed by radical chain pathways.[3,15] When organic reagents such as galvinoxyl or nitrosodurene are added to the reaction solutions, reaction proceeds much more rapidly. Since both these substances are quite stable, it is not evident a priori that reaction 5 (or its counterpart with R· replaced by a spin trap R that generates a stable radical RH·) should proceed. We observe that in the absence of substituting ligand L, reaction of stoichiometric quantities of either galvinoxyl or nitrosodurene with the parent hydride **1** leads to formation of dimer, **3**. This reaction probably proceeds via hydrogen abstraction from **1**, eq 5, followed by coupling of the metal carbonyl radicals. Benzoyl peroxide at 55 °C and the spin trap, phenyl-*tert*-butylnitrone, seem to be less active in initiating the chain substitution process. Correspondingly, the stoichiometric reaction of either of these substances with hydride was not observed to occur readily.

In studies of the substitution of $HRe(CO)_5$, photolysis in the presence of a small amount of $Re_2(CO)_{10}$ served to promote the substitution reaction, presumably by generating $Re(CO)_5\cdot$ radicals via homolysis of the Re–Re bond.[2] It has been established that 550-nm irradiation of **3** or **4** results in efficient homolysis of the metal–metal bond.[11,16–18]

We observe that in the absence of added **3**, irradiation of a solution of **1** plus PBu_3 with 500-nm light has no effect. However, when the dimer is present in concentration only a few percent of the concentration of **1**, irradiation causes rapid formation of the substitution product, **1**-PBu_3. The fact that the overall quantum yield for this reaction is at least 1000 indicates that the chain lengths involved in the series of reactions 6 through 8 are on the order of 2000 or greater. This follows from the fact that the quantum yield for formation of solvent-separated radicals $W(CO)_3(\eta^5\text{-}C_5H_5)\cdot$ on irradiation of the dimer are no higher than 0.4–0.6, as judged by quantum yields for formation of **5** when **3** is irradiated in the presence of halogen donors.[11,18,19]

Such a long chain length indicates that chain termination steps are unimportant. It is not surprising then that we observe no evidence of formation of dimers in the substitution reactions. The long chain length also suggests that the substitution process, eq 6 and 7, must occur with facility. These results are consistent with other observations that suggest that the metal carbonyl radicals with 17 electrons in the metal valence orbitals are especially labile.[20] The present results are interesting in that they involve a substituted carbonyl species with only three CO groups on the metal. If the $\eta^5\text{-}C_5H_5$ ring can be taken to occupy the equivalent of three coordination positions, then the radical species is six-coordinate. The present results are consistent with the observation that irradiation of either **3** or **4** results in formation of dimeric species $M_2(CO)_4(\eta^5\text{-}C_5H_5)_2$, with metal–metal triple bonds.[19] The radicals formed upon homolysis of the dimer presumably lose CO in a rapid reaction; the resulting 15-electron species couple to form the dimer with a multiple metal–metal bond.

The tricarbonyl(cyclopentadienyl)metal dimers **3** and **4** are especially attractive reagents for photoinitiation of radical chain processes in organometallic and organic chemistry. Homolysis of the dimers to form the desired radicals can be effected efficiently with relatively long wavelength (550 nm) irradiation. Thus, competing photochemical processes can in many cases be avoided. Among the transition-metal carbonyl radicals, both **3** and **4** are moderately reactive in radical abstraction processes.[21] Although the dimers are only slightly soluble in alkanes, they are more soluble in benzene and more polar solvents.

It is of interest that the substitution of **1** can also be photoinitiated by irradiation of **4**. The overall quantum yield for substitution does not appear to be as large as observed when **3** was used but is nevertheless much greater than 1. That the abstraction of H from **1** by $Mo(CO)_3(\eta^5\text{-}C_5H_5)$ does not occur readily is evident from the observation that **2** is not formed in observable concentrations upon irradiation with 500-nm light of a solution of **1** and **4**. By contrast, irradiation of a solution of **2** and **3** results in formation of **1**. That is, when M = Mo and M′ = W, reaction 3 proceeds to the right on photolysis. These observations are generally consistent with the supposition that the W–H bond energy is larger than the Mo–H bond energy.[22,23]

We have alluded above to the observation that irradiation of a solution of **1** plus PBu_3 at 500 nm produced no evidence of increased substitution rate, whereas irradiation at wavelengths shorter than 400 nm did promote the substitution. By use of 311-nm light the quantum yield for overall substitution was measured to be in the range from 6 to 30, suggesting a radical chain mechanism. It is reasonable to suppose that the 311-nm irradiation causes homolysis of the W–H bond with low quantum yield, eq 11. The observation that irradiation

$$HW(CO)_3(\eta^5\text{-}C_5H_5) + h\nu \rightarrow H + W(CO)_3(\eta^5\text{-}C_5H_5) \tag{11}$$

of **1** in the presence of trityl chloride leads to complete conversion to **5** supports this contention. To our knowledge, this represents the first example of photolysis of a single transition metal–hydrogen bond.[24] If the quantum yield for this process is low, the overall yield for photosubstitution will depend on the length of irradiation time and other variables of the system, because trace impurities can be expected to scavenge a substantial fraction of the metal-centered radicals first formed. Assuming a value of 30 for the overall quantum yield and assuming that the average chain length for the chain substitution is about 2000, the quantum yield for the primary photoprocess, eq 11, is on the order of 0.015, a not unreasonable value.[25]

Our results show that the thermal reaction of **2** with PBu_3 is at least 10^6 times faster than the analogous thermal reaction of **1**. The mechanism of the reaction is unknown. The thermal reaction is too fast to permit observations regarding promotion by use of photoinitiators or added radicals using the techniques readily available. The only other hydride for which substitution has been observed to occur with comparable rate is $HCo(CO)_4$.[27] In that case as well, the mechanism of the reaction is not clear. However, comparison with the observed substitution rates for other hydrides suggests that reaction via a nonradical pathway (i.e., CO dissociation, hydride migration, or an associative pathway) would proceed much more slowly than the observed rates. Assuming that a radical chain pathway is operative, substitution of **2** would be expected to be more rapid than for **1**, because the Mo–H bond should be substantially weaker than the W–H bond. This means that a wider range of species should be capable of initiating reaction. Once reaction is initiated, the $Mo(CO)_3(\eta^5\text{-}C_5H_5)\cdot$ radical formed may undergo more facile substitution. However, we do not know enough about the details of the individual steps in the radical chain process to account convincingly for the much more rapid reaction of **2** in terms of any particular overall mechanism for substitution.

The very marked dependence of the substitution rates of both **1** and **2** on the nature of the entering ligand is worthy of comment. It is especially interesting that substitution of **2** by $AsPh_3$ was not observed, even when the reaction mixture was irradiated in the presence of the dimer, **4**, which should be an extremely efficient photoinitiator. The marked ligand dependence in the substitution reactions is readily accounted for in the context of the radical chain process, in terms of eq 8. Since the competing chain termination steps that involve coupling of the radicals presumably have very large bimolecular rate constants,[16] the hydride exchange reaction, eq 8, must be fast to ensure a long chain. For this to be the case, the reaction cannot be significantly endothermic. We thus expect that hydride exchange will occur most rapidly for the case in which the metal–hydrogen bond in the substituted hydride possesses a higher bond dissociation energy than in the parent hydride. But the metal–hydrogen bond energy should be sensitive to the presence of other substituents on the metal. Although data regarding this question are not available for the compounds of interest here, it would appear from what is known in other cases, and on the basis of the kinetics results, that replacement of CO by a strongly nucleophilic ligand such as PBu_3 leads to a stronger M–H bond, whereas replacement by the much more weakly nucleophilic $AsPh_3$ results in no change or a weakening of the M–H bond. However, considerable additional work will be required to clarify this interesting aspect of the radical chain process.

Finally, the question remains whether there is an observable contribution from another, nonchain pathway for substitution into **1**. There are at least some indications of an alternative pathway which involves ligand dependence. The reactions seem to occur much more rapidly in the solutions prepared for NMR studies, in which concentrations are about an order of magnitude higher than in the solutions prepared for IR analysis. Secondly, the relative rates of reaction of **1** with a variety of ligands reveal a substantial dependence on ligand character; the most weakly nucleophilic ligands $AsPh_3$ and PPh_3 react more slowly than PBu_3 or $P(O\text{-}i\text{-}Pr)_3$. However, as we have seen, these results are not inconsistent with a radical chain process, because the length of the chain in the substitution may be governed in part by ligand nucleophilicity and concentration. We must conclude that at present it is not possible to say much regarding a nonradical pathway for reaction. At the very least, however, the result of Green and co-workers, especially the closely similar relative rates which bear on the kinetic isotope effect, must be viewed with reservations.

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Registry No. **1**, 12128-26-6; **1**-PBu_3, 65437-11-8; **1**-PPh_3, 33085-24-4; **1**-$P(O\text{-}i\text{-}Pr)_3$, 65392-06-5; **2**, 12176-06-6; **2**-PBu_3, 33479-96-8; **2**-$P(OEt)_3$, 61918-53-4; **3**, 12566-66-4; **4**, 12091-64-4; **5**, 12128-24-4.

References and Notes

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(25) There is not in evidence at the moment a promising means of spin trapping the proposed radicals. Experiments to detect $W(CO)_3(\eta^5\text{-}C_5H_5)\cdot$ generated by photolysis of **1** at 311 nm using ESR have not been attempted, because as we have indicated, nitrosodurene reacts with **1** in the dark, forming **3**. Nitroso-*tert*-butane is reported to form extremely light-sensitive adducts with manganese radicals.[26]

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