which serves as a key link in a redox chain reaction.

Acknowledgment. This work was supported by the National Science Foundation. The iridium used in these studies was provided on loan by Matthey Bishop, Inc.

Registry No. $[Ir(NH_3)_5acn](ClO_4)_3$, 73453-89-1; $[Ir(NH_3)_5bzn](ClO_4)_3$, 73453-87-9; [*trans*-$Ir(NH_3)_4I_2]_2S_2O_6$, 73495-00-8; $[Ir(NH_3)_5H_2O](ClO_4)_3$, 31285-82-2; $[Ir(NH_3)_5I](ClO_4)_2$, 67573-09-5; $Ir(NH_3)_5Cl^{2+}$, 29589-09-1; $Ir(NH_3)_5Br^{2+}$, 35884-02-7; $Ir(NH_3)_5I^{2+}$, 25590-44-7; *trans*-$Ir(NH_3)_4I_2^+$, 62153-22-4; *trans*-$Ir(NH_3)_4(H_2O)I^{2+}$, 73453-92-6; *trans*-$Ir(NH_3)_4Br_2^+$, 62153-21-3; *trans*-$Ir(NH_3)_4Cl_2^+$, 62153-20-2; $Ir(NH_3)_6^{3+}$, 24669-15-6; $Ir(NH_3)_5H_2O^{3+}$, 29589-08-0; $Ir(NH_3)_5acn^{3+}$, 73453-88-0; $Ir(NH_3)_5bzn^{3+}$, 53783-43-0; *trans*-$Ir(NH_3)_4(H_2O)Cl^{2+}$, 73453-91-5; *trans*-$Ir(NH_3)_4(H_2O)Br^{2+}$, 73453-90-4; *trans*-$Ir(NH_3)_4(H_2O)_2^{3+}$, 62153-23-5.

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Thermal and Photochemical Reactivity of $(C_5H_5)_2V_2(CO)_5$

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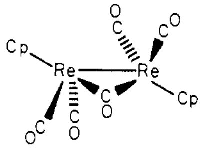
The complex $Cp_2V_2(CO)_5$ has been synthesized by photolysis of $CpV(CO)_4$ in tetrahydrofuran (THF). The sequence of reactions leading to dimerization has been shown to require photoinduced dimerization of the observed primary photoproduct $CpV(CO)_3(THF)$. The thermal and photochemical reactivity of $Cp_2V_2(CO)_5$ with CO and a variety of phosphines has been examined in order to assess the mechanistic significance of the V–V multiple bond and the carbonyl semibridges. On the basis of both chemical trapping experiments and low-temperature photolyses, it is found that strong nucleophiles may directly attack the pentacarbonyl dimer with displacement of the metal–metal double bond; monomeric products result. Weak nucleophiles effect net CO substitution on the intact dimer but do so via the species $Cp_2V_2(CO)_4$, which is in equilibrium with the pentacarbonyl; this equilibrium has been demonstrated by using ^{13}CO. A THF adduct of this tetracarbonyl dimer has been observed directly at low temperatures and proves that the primary chemical consequence of irradiation of $Cp_2V_2(CO)_5$ is CO dissociation, not dimer scission. The reaction of PEt_2Ph with dimeric, multiply bonded $Cp_2V_2(CO)_5$ thus exhibits a remarkable product dependence on the source of activation energy.

Introduction

The photochemistry of dimeric transition-metal carbonyl complexes containing a metal–metal bond of unit order exhibits substantial complexity.[1] Irradiation at the absorption frequency assigned as $\sigma \rightarrow \sigma^*$ (with respect to the metal–metal bond) might reasonably be expected to destroy that bond. Photolysis in the presence of alkyl halides has indeed yielded products which are consistent with (but do not in every case uniquely require) the photoproduction of the radical monomer M·.

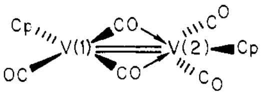
Photolysis of a complex containing a multiple metal–metal bond might well lead to distinctly different chemical consequences. Thus, a double-bonded dimer with a ground-state one-electron configuration $\sigma^2\pi^2$ will maintain a formal single bond following any one-electron excitation. In such a circumstance, ligand photodissociation, which dominates the photochemistry of monomeric metal carbonyls, might become competitive with or preferable to metal–metal bond homolysis. Even for the single-bonded dimer $[CpMo(CO)_3]_2$, a flash photolytic study has demonstrated[2] that Mo–Mo homolysis is accompanied by CO photodissociation. As indicated above, this complexity necessitates careful reconsideration of earlier studies which tended to demand a single and universal mechanism for the photochemistry of single-bonded dimers.

We report here a study of the thermal chemistry and photochemistry of $Cp_2V_2(CO)_5$.[3,4] We consider this to be an example of a complex with a double bond[5] between the metal atoms and thus a test case for our simple ideas on the photochemistry of this class. The intriguing geometric and electronic structure of $Cp_2V_2(CO)_5$[6] also motivated this study. The complex does not possess the symmetric structure of $Cp_2Re_2(CO)_5$[7] (I) but instead may be viewed as the fusion of $CpV(CO)_3$ and $CpV(CO)_2$ monomers. Two of the CO groups in the $CpV(CO)_3$ fragment participate in a structurally and spectroscopically significant interaction with the second metal atom ("carbonyl semibridges"[4,6]).

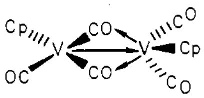


I

Detailed comparison of structural parameters for $Cp_2V_2(CO)_5$ and $Cp_2V_2(CO)_4(PPh_3)$ has been used[8] in an attempt to support the idea that the carbonyl semibridges in both of these molecules are performing a donor function toward V(2) (structure II). This model leads to an 18-electron configuration at both V(1) and V(2), provided the net effect of two donor semibridges is the donation of only two electrons. The acceptor semibridge model[6] (III), on the other hand, yields a 16-electron configuration at both metal atoms. The ex-



II



III

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(1) Wrighton, M. S. *Top. Curr. Chem.* **1976**, *65*, 37.

(2) Hughey, J. L.; Bock, C. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1975**, *97*, 4440.

(3) Fischer, E. O.; Schneider, R. J. *Chem. Ber.* **1970**, *103*, 3685.

(4) Cotton, F. A.; Frenz, B. A.; Kruczynski, L. *J. Am. Chem. Soc.* **1973**, *95*, 951.

(5) This statement contrasts with that published previously.[6] In support of our claim, the chromium–chromium triple-bond length in $Cp_2Cr_2(CO)_4$ is 2.22 Å. Since vanadium is intrinsically larger than chromium by as much as 0.08 Å (the difference between the M–C(Cp) distances in the two compounds), the V–V separation of 2.46 Å in $Cp_2V_2(CO)_5$ supports the idea of V–V multiple bonding.

(6) Cotton, F. A. *Prog. Inorg. Chem.* **1976**, *21*, 1.

(7) Foust, A. S.; Hoyano, J. K.; Graham, W. A. G. *J. Organomet. Chem.* **1971**, *32*, C65.

(8) Huffman, J. C.; Lewis, L. N.; Caulton, K. G., submitted for publication in *Inorg. Chem.*

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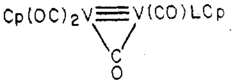
periments described here were designed to test for the presence or absence of an unsaturated metal center in $Cp_2V_2(CO)_5$, thus providing an operational test for distinguishing between these bonding models.

Finally, we were intrigued by the possibility that the multiple bond in $Cp_2V_2(CO)_5$ could lead to enhanced reactivity such as occurs on passing from $Cp_2Mo_2(CO)_6$ to $Cp_2Mo_2(CO)_4$. For the dimeric molybdenum tetracarbonyl, ligand addition is the exclusive model of reaction, with concomitant reduction in metal–metal bond order from three to one.[9] The corresponding reduction of a double metal–metal bond in $Cp_2V_2(CO)_5$ should produce monomeric products.[10]

Underlying all of this is our interest in the possibility of observing a substitution product $Cp_2V_2(CO)_4L$ whose structure has reverted to the μ_2-CO type (IV), analogous to that of $Cp_2Re_2(CO)_5$.



IV

Experimental Section

General. All operations were performed under an atmosphere of nitrogen, by using either Schlenk techniques or a Vacuum Atmospheres glovebox. Solvents, dried over benzophenone/sodium/potassium, were degassed by vacuum transfer.

The photolyses described below utilize a 550-W medium-pressure mercury lamp (Hanovia) held vertically in a water-cooled immersion well of outer diameter 5.5 cm. In order to effect maximum utilization of the output of this lamp in the synthesis of $Cp_2V_2(CO)_5$, we placed the solution of $CpV(CO)_4$ in a toroidal reactor which contains this solution wholly in the region of space in which the lamp emits; the Pyrex reactor is 16 cm tall, with the upper 6 cm devoted to Schlenk fittings for loading and degassing the reactor. For irradiation of small volumes to be possible, the "path length" of the reactor is only 0.9 cm. Photodissociated CO may be swept away by a nitrogen purge via a long syringe needle which also serves to agitate the solution. Because all fittings are at the top of the reactor, irradiations may be carried out with the reactor and lamp in any cold bath which might be required.

Spectroscopic experiments with thermally unstable compounds were carried out in a low-temperature infrared cell of local construction. Irradiation was carried out in this cell, which consisted of a vacuum-jacketed cold finger whose lower end was a solution infrared cell fabricated from brass. Cell windows were BaF_2 or NaCl, with NaCl windows on the outer vacuum jacket. The cell (0.1 mm) incorporated access tubes which allowed evacuation of or introduction of gases to the loaded cooled cell. Dry ice was used in conjunction with acetone (−78 °C) or acetonitrile (−42 °C).

Photochemical substitution reactions were carried out in 17-mm od, Pyrex reaction tubes capped with septa. Two syringe needles, one of which reached to the bottom of the tube, permitted a N_2 purge during irradiation. Failure to remove CO in this manner results in greatly reduced yields. The mercury-vapor lamp and the reaction tube were immersed in flowing water (10–15 °C).

All thermal reactions were performed in a glovebox under nitrogen at room temperature. The progress of reactions was monitored by using infrared spectroscopy. For preparative experiments at low temperature, reaction tubes were immersed in (and irradiated through) a dry ice/acetonitrile bath.

$Cp_2V_2(CO)_5$. $CpV(CO)_4$ (0.788 g, 3.5 mmol) was dissolved in 25 mL of dry degassed THF. This orange solution was placed in the toroidal reactor (maintained below 25 °C in a water bath) and photolyzed, under a nitrogen purge, for 100 min. The resultant green solution was filtered (no solid was evident) and placed in a cylindrical sublimer 6 cm in diameter. The THF was then removed by vacuum transfer of solvent out of the sublimer itself. Sublimation (5×10^{-3} torr, dynamic vacuum) at room temperature transports 0.3 g of unchanged $CpV(CO)_4$ to the water-cooled probe; trace quantities of $Cp_2V_2(CO)_5$ also sublime. The material on the probe is removed for reuse. The material which does not sublime is extracted with hexanes (ca. 40 mL), the hexane solution is filtered, and the solvent is rotary-evaporated to yield emerald green crystals (0.300 g, 75% yield with 62% conversion). The product was identified by its mass spectrum[3] (parent ion and successive loss of five CO ligands) and infrared spectrum (2005 (m), 1950 (s), 1900 (m), 1869 (m), 1828 (s) cm^{-1}; in hexanes). The proton NMR at 220 MHz shows a single Cp resonance at τ 5.57 (in C_6D_6); no quadrupolar broadening (^{51}V) is evident. These spectral observations agree well with those reported earlier.[3]

The irradiation time noted above is optimum for the solution cell described. Since $Cp_2V_2(CO)_5$ is itself photosensitive, changes in irradiation geometry will require alteration of the photolysis time.

$Cp_2V_2(CO)_5$ + PPh_3. $Cp_2V_2(CO)_5$ (0.05 g, 0.13 mmol) and PPh_3 (0.026 g, 0.1 mmol) were combined in 8 mL of THF.

a. Thermal Reaction. Half of this solution was allowed to stand at room temperature. After 1 h, approximately 10% conversion to $Cp_2V_2(CO)_4PPh_3$ is evident by an infrared peak at 1770 cm^{-1} (see below). No bands due to $CpV(CO)_3PPh_3$ or $CpV(CO)_4$ were noted. After 9 h (about 70% conversion), IR bands of $Cp_2V_2(CO)_4(PPh_3)$ have not increased in intensity and peaks due to $CpV(CO)_3PPh_3$ and $CpV(CO)_4$ are evident.

b. Photochemical Reaction. The other half of the above reaction solution was photolyzed in a Pyrex tube and with N_2 flushing through the solution. Infrared analyses of the solution after 5 min of photolysis shows that $Cp_2V_2(CO)_4PPh_3$ has been produced (approximately 50% conversion). Photolysis for an additional 5 min leads to almost complete conversion to $Cp_2V_2(CO)_4PPh_3$[3] with traces of $CpV(CO)_3PPh_3$ and $CpV(CO)_4$ now evident.

$Cp_2V_2(CO)_4PPh_3$ produced by photolysis (30 min) on a larger scale (0.15 g, 0.4 mmol, of $Cp_2V_2(CO)_5$ and 0.1 g, 0.4 mmol, of PPh_3 in 10 mL of THF) was precipitated by slow addition of hexanes and crystallized from benzene by slow addition of hexanes: IR (THF) ν(CO) 1930, 1870, 1820, 1770 cm^{-1}; ^1H NMR (C_6D_6) τ 5.67 (s), 5.11 (d, J(PH) = 2 Hz); mass spectrum $Cp_2V_2(CO)_nPPh_3^+$, n = 1–3, as well as smaller fragments (i.e., parent ion not seen at 70 eV and a sample temperature of 218 °C). These values agree satisfactorily with those reported earlier.[3] The final identity of this compound was established by using X-ray crystallography.[8]

$Cp_2V_2(CO)_5$ + $(Ph_2P)_2CH_2$. a. Photochemical Reaction. Irradiation (15 min) of a saturated THF solution of $Cp_2V_2(CO)_5$ containing equimolar $Ph_2PCH_2PPh_2$(dpm) results in the appearance of four CO stretching frequencies (1931, 1868, 1822, 1771 cm^{-1}) characteristic of $Cp_2V_2(CO)_4$(dpm). Also produced in lesser quantity is $CpV(CO)_3$(dpm), ν(CO) = 1953, 1880, and 1850 cm^{-1} in hexane;[11] this compound was shown to be a secondary photolysis product by observing its formation on photolysis of pure $Cp_2V_2(CO)_4$(dpm). The THF was removed from the photolyzed solution under vacuum. $CpV(CO)_3$(dpm) is separated from the residual solids by extraction with hexane; solid $Cp_2V_2(CO)_4$(dpm) remains. The inequivalence of the phosphorus nuclei (one coordinated and one free) was evident in the proton NMR of $CpV(CO)_3$(dpm): τ 5.35 (C_5H_5, d, J(PH) = 1 Hz), 6.94 (CH_2, d, J(PH) = 5 Hz, J(P′H) not observed). The ^{31}P NMR ($CDCl_3$) of this compound in hexane at −40 °C showed a sharp doublet (J(PP) = 49 Hz) at −27.6 ppm due to the uncoordinated phosphorus (free dpm appears at −24.8 ppm) and an exceptionally broad resonance (full width approximately 1100 Hz) at about +47 ppm due to phosphorus bound to quadrupolar ^{51}V.

$Cp_2V_2(CO)_4$(dpm) decomposes to $CpV(CO)_3$(dpm) and $CpV(CO)_2$(dpm) when passed through silica gel; $CpV(CO)_3$(dpm) partially decomposes to $CpV(CO)_2$(dpm) as well under similar treatment. $CpV(CO)_2$(dpm) was characterized by CO stretching frequencies (in THF) at 1870 and 1805 cm^{-1}. Both $CpV(CO)_3$(dpm) and $CpV(CO)_2$(dpm) were characterized by mass spectroscopy; in each case the highest mass seen corresponded to $CpV(CO)_2(dpm)^+$. $Cp_2V_2(CO)_4$(dpm) showed no masses higher than $Cp_2V_2CO(dpm)^+$ in the electron-impact mass spectrum; the proton NMR spectrum in C_6D_6 showed, in addition to phenyl resonances, resonances at τ 5.67 (C_5H_5, s), 5.05 (C_5H_5, d, J(PH) = 3 Hz), and 6.76 (CH_2, d, J(PH) = 7 Hz).

b. Thermal Reaction. $Cp_2V_2(CO)_5$ (0.025 g, 0.07 mmol) and dpm (0.025 g, 0.07 mmol) were combined in 4 mL of THF. After 9 h at 25 °C, the formation of $CpV(CO)_3$(dpm) and $Cp_2V_2(CO)_4$(dpm)

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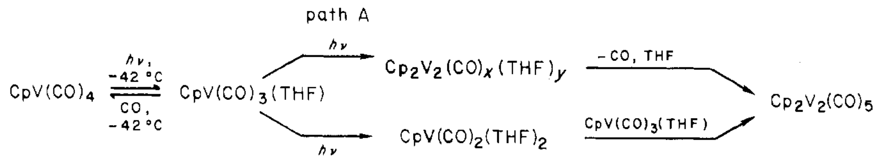
(9) Curtis, M. D.; Klingler, R. J. *J. Organomet. Chem.* **1978**, *161*, 23.

(10) For the results of an earlier study of the reactions of $Cp_2V_2(CO)_5$ with Lewis bases, see ref 3.

(11) Rehder, D.; Dahlenburg, L.; Muller, I. *J. Organomet. Chem.* **1976**, *122*, 53.

Scheme I



was evident (IR spectrum). The monomeric product can be extracted out of the dried reaction mixture with hexanes, leaving only green $Cp_2V_2(CO)_4(dpm)$, which is soluble in THF. Both products were characterized as above.

$Cp_2V_2(CO)_5$ + $Ph_2P(CH_2)_2PPh_2$(dppe). $Cp_2V_2(CO)_5$ (0.100 g, 0.26 mmol) was combined with dppe (0.424 g, 1.08 mmol) in 6 mL of THF. The solution, maintained at 25 °C for 6 h, turned red. The infrared spectrum of the solution exhibited carbonyl bands (1945 (s), 1863 (s), 1845 (m), 1795 (m) cm^{-1}) characteristic[11] of a mixture of $CpV(CO)_3$(dppe) and $CpV(CO)_2$(dppe). The solvent was removed under vacuum and a portion of the solid residue was dissolved completely in C_6D_6. The relative yield of the monomeric products $CpV(CO)_3$(dppe) and $CpV(CO)_2$(dppe) was determined to be 1.02:1.00 by integration of the cyclopentadienyl resonances: ^1H NMR $CpV(CO)_3$(dppe) τ 5.67 (C_5H_5, doublet, $J(PH) = 1$ Hz); $CpV(CO)_2$(dppe), τ 5.97 (C_5H_5, triplet, $J(PH) = 1$ Hz).

$Cp_2V_2(CO)_5$ + PEt_2Ph. a. Exploratory. $Cp_2V_2(CO)_5$ (0.2 g, 0.54 mmol) and PEt_2Ph (1 mL of a 0.5 M solution in THF) were combined in 16 mL of hexanes. Half of this solution was maintained at 25 °C. Production of $CpV(CO)_3(PEt_2Ph)$ was evident in the IR spectrum immediately after addition of the phosphine solution. The solution color changed from green to red in 5 h, the products being $CpV(CO)_3(PEt_2Ph)$ and $CpV(CO)_2(PEt_2Ph)_2$ (established from the IR and ^1H NMR patterns); the mole ratio of these monomeric products (NMR assay) was 1.5:1. The other half of this reaction solution was photolyzed for 10 min. The major product in solution was $CpV(CO)_3(PEt_2Ph)$. The results were comparable in THF as solvent. In hexane only a green precipitate formed during photolysis; this was identified as $Cp_2V_2(CO)_4(PEt_2Ph)$ by comparison of its ^1H NMR and IR spectra to those of $Cp_2V_2(CO)_4PPh_3$.

b. Thermal Reaction. The following reaction was carried out with a stoichiometry more consistent with the products determined above. $Cp_2V_2(CO)_5$ (0.026 g, 0.07 mmol) and PEt_2Ph (1 mL of a 0.28 M solution in hexanes) were combined in 5 mL of hexanes and held at 25 °C for 4 h. Proton NMR assay of the dried reaction residues, taken up completely in C_6D_6, showed the Cp ring doublet of $CpV(CO)_3(PEt_2Ph)$ and the corresponding triplet of $CpV(CO)_2(PEt_2Ph)_2$ (only the cis isomer was detected) with a mole ratio of 1.2:1.0.

c. Photochemical Reaction. PEt_2Ph (1 mL of a 0.28 M solution in hexanes) was slowly added to a cold (−50 °C) solution of $Cp_2V_2(CO)_5$ (0.1 g, 0.27 mmol) in 10 mL of THF. Half of this solution was maintained at −50 °C (without irradiation) for 30 min; at the end of this time, the infrared spectrum confirmed that no reaction has taken place. The other half of this solution was photolyzed in a Pyrex tube at −50 °C, with a concurrent N_2 flush. Photolysis for 20 min results in approximately 90% conversion to $Cp_2V_2(CO)_4(PEt_2Ph)$; this is the only product detected: IR (THF) ν(CO) 1920, 1860, 1820, 1770 cm^{-1}; ^1H NMR (C_6D_6, Cp resonances) τ 5.57 (s), 5.16 (d, $J(PH) = 2$ Hz).

$Cp_2V_2(CO)_4(PEt_2Ph)$ + PEt_2Ph. Photolysis (25 °C, 10 min) of a THF solution of $Cp_2V_2(CO)_4(PEt_2Ph)$, alone or in the presence of excess PEt_2Ph, produces no monomeric products. A solution of phosphine-substituted dimer does decompose in the absence of phosphine over a period of 5 days to give $CpV(CO)_3(PEt_2Ph)$ as the major product and $CpV(CO)_2(PEt_2Ph)_2$ as the minor product.

Thermal Substitution on $CpV(CO)_4$. $CpV(CO)_4$ (0.067 g, 0.3 mmol) and PEt_2Ph (2 mL of a 0.29 M solution in hexanes) were combined in 5 mL of THF. The solution was permitted to stand at 25 °C. In 4 h, there was no detectable (IR) conversion to $CpV(CO)_3(PEt_2Ph)$.

Results

Synthesis of $Cp_2V_2(CO)_5$. The primary photochemical step in the synthesis of $Cp_2V_2(CO)_5$ employed here is photodissociation of CO from $CpV(CO)_4$ to produce a tricarbonyl species. Spectral evidence for such a species was sought but not found at 25 °C. The vanadium concentration was purposely kept high in all synthetic reactions in order to encourage a bimolecular reaction leading to the dimeric product. This would prevent the steady-state concentration of a tricarbonyl complex from achieving a detectable level. Photolysis of a dilute (10^{-3} M) solution of $CpV(CO)_4$ in THF at 20 °C for 20 min yielded a solution with *no* carbonyl frequencies; the tricarbonyl fragment thus decomposes if it fails to encounter a second metal fragment during its limited lifetime. Irradiation of a dilute THF solution of $CpV(CO)_4$ in an infrared cell at −42 °C, with periodic evacuation of evolved gas, caused essentially complete conversion to a green species exhibiting two vibrational bands in the terminal carbonyl region (1952, 1838 cm^{-1}). The similarity of the observed vibrational frequencies to those of $CpV(CO)_3PPh_3$ supports identification of this species as $CpV(CO)_3$(THF). This species reverts to $CpV(CO)_4$ on addition of CO to the cell at −42 °C. The possibility that formation of $Cp_2V_2(CO)_5$ results from coupling of $CpV(CO)_3$(THF) and $CpV(CO)_4$ was investigated by slowly warming a CO-free solution containing a 2:1 molar ratio of $CpV(CO)_3$(THF) and $CpV(CO)_4$ from −42 to −19 °C. This had the effect of causing bands due to $CpV(CO)_3$(THF) to disappear without the formation of *any* new carbonyl complex. Thermal coupling of these monomeric species is thus not feasible in the temperature region studied, due probably to the kinetic inertness of $CpV(CO)_4$. Support for the idea that dimerization does not involve $CpV(CO)_4$ comes from lengthy irradiation experiments at −78 °C. As stated above, it is possible to produce $CpV(CO)_3$(THF) solutions containing essentially no $CpV(CO)_4$ at −78 °C. Nevertheless, further irradiation of such a solution at −42 °C results in formation of $Cp_2V_2(CO)_5$, no further intermediates being observed. The overall sequence of reactions is summarized in Scheme I, which emphasizes that $Cp_2V_2(CO)_5$ formation requires *two* photochemical steps; thermal dimerization of $CpV(CO)_3$(THF) to $Cp_2V_2(CO)_5$ does not compete successfully with its complete decarbonylation. Scheme I leaves open the question of whether the second photon activates $CpV(CO)_3$(THF) toward dimerization (path A) or effects decarbonylation followed by thermal dimerization (path B).

We anticipated that a superior synthesis might result if authentic $CpV(CO)_3$ could be produced by irradiation in hexanes at 20 °C. Although $Cp_2V_2(CO)_5$ is produced in this manner, this is a far slower reaction than that in THF. This solvent effect may be due to rapid recombination of $CpV(CO)_3$ with CO in the solvent cage, since gross decomposition does not occur on photolysis of $CpV(CO)_4$ in hexanes. A nitrogen purge greatly improves the synthesis, even in THF.

The synthesis described here has been optimized for yield of $Cp_2V_2(CO)_5$. Longer irradiation results in a decreased yield. We have verified that irradiation of pure $Cp_2V_2(CO)_5$ in THF at 25 °C under a N_2 purge results in destruction of dimer. Under these conditions $CpV(CO)_4$ is the only carbonyl complex formed by irradiation of $Cp_2V_2(CO)_5$. The coproduct, a THF-soluble cyclopentadienylvanadium cluster, is under further investigation.

Thermal Reactions of $Cp_2V_2(CO)_5$. Dimeric $Cp_2V_2(CO)_5$ reacts with various phosphines at 25 °C in THF according to eq 1–3. Qualitatively, the rates of these reactions depend on

$$Cp_2V_2(CO)_5 + PPh_3 \rightarrow Cp_2V_2(CO)_4PPh_3 \quad (1)$$

$$Cp_2V_2(CO)_5 + Ph_2PCH_2PPh_2 \rightarrow Cp_2V_2(CO)_4(Ph_2PCH_2PPh_2) \quad (2)$$

$$Cp_2V_2(CO)_5 + 4PEt_2Ph \rightarrow CpV(CO)_3PEt_2Ph + cis\text{-}CpV(CO)_2(PEt_2Ph)_2 \quad (3)$$

the identity of the phosphine, consistent with an associative mechanism. In reactions which proceed to monomeric products at 25 °C, it is possible to show that the reaction stoichiometry is totally conservative of CO ligands. Thus, an excess of PEt_2Ph captures both the dicarbonyl and tricarbonyl fragments (eq 3, established by NMR integration). Excess $Ph_2P(CH_2)_2PPh_2$ likewise quantitatively captures the monomeric fragments as $CpV(CO)_3(dppe)$ and $CpV(CO)_2(dppe)$. The former compound contains a monodentate "dangling" phosphine.

Three mechanisms (eq 4–6) are consistent with these observations on the thermal reactions of the dimer.

$$Cp_2V_2(CO)_5 \xrightarrow{L} [Cp_2V_2(CO)_5L]^{*} \rightarrow \text{products} \quad (4)$$

$$Cp_2V_2(CO)_5 \rightleftharpoons CpV(CO)_2 + CpV(CO)_3 \xrightarrow{L} \text{products} \quad (5)$$

$$Cp_2V_2(CO)_5 \rightleftharpoons CO + Cp_2V_2(CO)_4 \xrightarrow{L} \text{products} \quad (6)$$

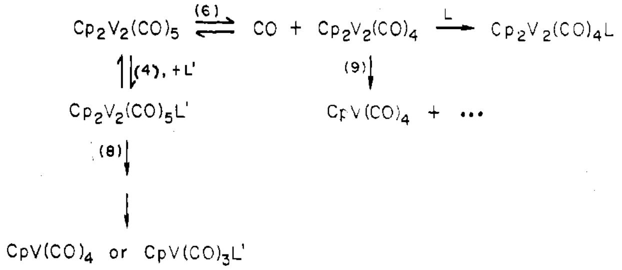
Equation 5, preequilibrium scission of the dimer, is unlikely in view of the production of dimeric substitution products with L = PPh_3 and $Ph_2PCH_2PPh_2$. The bidentate chelate in particular should ring-close to $CpV(CO)_2(dpm)$ on every reactive encounter with $CpV(CO)_2$. The formation of dimeric products is more readily explained by path 4 or 6.

Selecting from among mechanisms 4–6 is possible on the basis of an examination of the reactivity of $Cp_2V_2(CO)_5$ toward CO. The pentacarbonyl dimer is a rather fragile molecule, even in the absence of nucleophiles. Under an atmosphere of purified nitrogen in a closed system, decomposition of $Cp_2V_2(CO)_5$ in hexane begins to be detectable within 10 min. The only carbonyl-containing product of this reaction is $CpV(CO)_4$. Flushing N_2 through a hexane solution of $Cp_2V_2(CO)_5$ accelerates the rate of this thermal reversion to monomer, consistent with a mechanism dissociative in CO. Conversely, if the hexane solution is flushed with CO in order to maintain a relatively high and constant concentration of this species, the rate of decomposition is depressed. Since added CO would seem to improve the *stoichiometry* of a reaction such as eq 7, the observation that added CO suppresses decomposition to monomer strongly indicates that dimer decomposition is preceded by an equilibrium step dissociative in CO (i.e., eq 6). This is wholly inconsistent with the mechanism in eq 5, since the monomeric fragments would rapidly capture CO; added CO would increase the rate of disappearance of dimer and/or the rate of appearance of $CpV(CO)_4$.

$$Cp_2V_2(CO)_5 + 3CO \rightarrow 2CpV(CO)_4 \quad (7)$$

It is possible to further demonstrate that the CO-deficient species which precedes rate-determining dimer decomposition is indeed in equilibrium with $Cp_2V_2(CO)_5$. If a hexane solution of the dimer is vigorously stirred in the presence of 1 atm of ^{13}CO, decomposition proceeds at the reduced rate described above. If this reaction is halted prior to completion, recovered pentacarbonyl dimer is found to be labeled with ^{13}CO (mass spectral evidence). The infrared spectrum of the labeled dimer permits the conclusion that the label has been scrambled completely among the three inequivalent CO environments. This was deduced by the appearance of frequencies qualitatively consistent with ^{13}CO in unique terminal (1955 cm^{-1}) and semibridge (1797 cm^{-1}) environments. A more complete vibrational analysis of the time evolution of dimer isotopomers during treatment with ^{13}CO, including interaction force constants between carbonyl ligands on different metals, provided quantitative confirmation for this conclusion. Vibrational bands due to doubly labeled molecules were also detected after 3 h. This scrambling of label is a consequence of the intramolecular carbonyl migration which causes ^1H NMR equivalence of the C_5H_5 resonances and precludes any attempt at ascertaining which CO is lost in the preequilibrium shown in eq 6.

Scheme II



L = THF, PPh_3, dpm; L′ = PEt_2Ph

The complete set of observations noted above is explicable in terms of Scheme II. The observed dependence of the decomposition rate on [CO] indicates that the sequence (6) + (9) is the kinetically significant path to $CpV(CO)_4$ in the presence or absence of added CO. The associative sequence (4) + (8) does not result in significant yields of monomer (reaction 4 is not ruled out as a *second* ^{13}CO-enrichment mechanism). The fact that some decomposition is still detected under 1 atm CO permits the conclusions

$$k_{-6}[CO] \approx k_9 \quad \text{or} \quad k_{-6} \gg k_9$$

Thus the intrinsic reactivity of the tetracarbonyl $Cp_2V_2(CO)_4$ toward CO greatly exceeds its tendency to decompose to $CpV(CO)_4$. From this it is readily deduced that this unsaturated species would be quite reactive toward even weak nucleophiles, which is consistent with the dimeric substitution products observed with $Ph_2PCH_2PPh_2$ and PPh_3.

On the other hand, path (4) + (8) may be detected and is the kinetically significant path for more basic phosphines. Thus, PEt_2Ph reacts rapidly with $Cp_2V_2(CO)_5$ at 25 °C to produce monomeric products (eq 3). This reaction does not proceed (via eq 4) through the dimeric intermediate $Cp_2V_2(CO)_4(PEt_2Ph)$. Independent (photochemical) synthesis of this compound (see below) allows examination of its reactivity toward phosphine (eq 10). Since this dimer is found to be unchanged on treatment with PEt_2Ph at 25 °C, its intermediacy in eq 3 is precluded; it follows that eq 3 occurs by the associative path 4. This same stability of $Cp_2V_2(CO)_4(PEt_2Ph)$ permits the conclusion that the rate of CO loss from the species $Cp_2V_2(CO)_5(PEt_2Ph)$ is negligible relative to its rate of "fragmentation" (see Discussion) to monometallic species. Both associative and dissociative mechanisms are thus available to $Cp_2V_2(CO)_5$, the distinction being dependent on the properties of the attacking nucleophile; the pentacarbonyl dimer thus exhibits a mechanistic selectivity toward Lewis bases.

$$Cp_2V_2(CO)_4(PEt_2Ph) + PEt_2Ph \not\rightarrow CpV(CO)_2(PEt_2Ph)_2 + CpV(CO)_3(PEt_2Ph) \quad (10)$$

Photochemical Reactivity. Irradiation of a solution containing $Cp_2V_2(CO)_5$ and $Ph_2PCH_2PPh_2$(dpm) leads to the same dimeric substitution product observed in the thermal reaction (eq 2), but at a greatly accelerated rate.

Several attempts to examine the photochemical reaction of equimolar $Cp_2V_2(CO)_5$ with PEt_2Ph at 25 °C in THF gave only confusing results because significant quantities of $Cp_2V_2(CO)_5$ are consumed in the rapid thermal reaction. The monomeric products of this thermal reaction complicate the carbonyl region of the infrared spectrum, and reproducibility was frustrated by varying time intervals prior to irradiation. The situation is somewhat simpler in hexane solvent, since the thermal reaction is slower and some of the authentic photoproduct $Cp_2V_2(CO)_4(PEt_2Ph)$ precipitates from the reaction solution, thereby facilitating its detection.

It is possible to quench the thermal reaction and thereby simplify the study of the photochemical reaction in THF. If a solution of the phosphine is added slowly to a cold (−50 °C) THF solution of $Cp_2V_2(CO)_5$, no detectable thermal reaction takes place on the time scale of the irradiation experiment. Under these conditions, irradiation yields only the product of CO substitution on the dimer (eq 11).

$$Cp_2V_2(CO)_5 + PEt_2Ph \xrightarrow[-50\ ^\circ C]{h\nu} Cp_2V_2(CO)_4(PEt_2Ph) + CO \quad (11)$$

As in the thermal reactions, examination of the fate of $Cp_2V_2(CO)_5$ upon irradiation under CO provides information on existing preequilibria. Purging a hexane solution of the dimer with N_2 during irradiation accelerates decomposition to $CpV(CO)_4$ (and carbonyl-free products) relative to the conversion of a sample comparably treated in the dark. If the experiment is repeated under a CO purge, decomposition is diminished compared to the irradiated, N_2-flushed sample. Irradiation under CO causes more decomposition than does CO treatment in the dark, however. Taken together, these observations imply that the chemically significant photochemical event is dissociation of CO; the equilibrium in eq 6 is photochemically driven so as to increase the steady-state concentration of $Cp_2V_2(CO)_4$. If, as proposed, the rate-determining step in dimer decomposition is first order in $[Cp_2V_2(CO)_4]$, the experimental observations are readily explained. Specifically excluded by the stabilizing effect of CO on photodecomposition is light-induced dimer scission (eq 5) or the production of some activated but intact dimer (e.g., a species free of carbonyl bridges such as V) which is susceptible to scission by CO (eq 12).

$$Cp_2V_2(CO)_5 \xrightarrow{h\nu} \underset{\mathrm{V}}{Cp(OC)_3V{=}V(CO)_2Cp} \xrightarrow{CO} 2CpV(CO)_3 \xrightarrow{+CO} 2CpV(CO)_4 \quad (12)$$

Solvent Effects. The spontaneous thermal decomposition of $Cp_2V_2(CO)_5$ at 25 °C is substantially slower in THF than in hexane. In view of the demonstrated activity of THF in the photochemical synthesis of the dimer, we have further investigated this solvent stabilization of $Cp_2V_2(CO)_5$.[12] The observed stabilization could result from production of $Cp_2V_2(CO)_4(THF)$ in reaction 6, with this species being more stable than $Cp_2V_2(CO)_4$ to reaction according to step 9. Conditions have been found under which the proposed THF adduct may be directly observed. Irradiation of $Cp_2V_2(CO)_5$ in THF at −78 °C in a low-temperature infrared cell produces a new species with four carbonyl vibrational frequencies (1925, 1845, 1820, 1770 cm^{-1}). The similarity of these frequencies to those of $Cp_2V_2(CO)_4(PPh_3)$ supports our assignment of this molecule as $Cp_2V_2(CO)_4(THF)$.

A study of the effect on $Cp_2V_2(CO)_5$ decomposition of the addition and removal of CO proved to be enlightening. Over the span of 5 min at 25 °C, a solution of $Cp_2V_2(CO)_5$ in THF showed negligible decomposition to $CpV(CO)_4$. Flushing a second portion taken from the same stock solution for 5 min with N_2 had *no* effect. Flushing a third portion of the stock solution with CO for 5 min gave substantial (approximately 20%) conversion to tetracarbonyl monomer. These effects are *opposite* to those observed in hexane and indicate that, in THF, the reaction sequence (6) + (9) is effectively nullified on the time scale of our experiments. Enhanced decomposition in the presence of added CO must then result from an associative reaction (path 4 + 8 with L′ = CO and/or THF). Use of a coordinating solvent thus efectively eliminates the kinetic significance of the thermal decomposition mechanism operative in hexane, leaving only the slower associative process to occur.

As in hexane, however, irradiation enhances decomposition. Irradiation of $Cp_2V_2(CO)_5$ in THF under a flow of nitrogen for 5 min produces about 13% decomposition to monomer. Photodissociation of CO thus increases the concentration of $Cp_2V_2(CO)_4(THF)$ to the point where path (3) + (4) becomes a significant contributor to the overall decomposition rate.

Discussion

Synthesis of $Cp_2V_2(CO)_5$. The original synthesis[3] of $Cp_2V_2(CO)_5$ involves acidification of $CpV(CO)_3^{2-}$ with aqueous HCl. Protonation of the dianion with 1 equiv of water produces[13] the isolable monohydride $CpV(CO)_3H^-$. Addition of a second proton would generate the (undetected) hydride $CpV(H)_2(CO)_3$, which must be unstable toward loss of H_2. The resultant metallic fragment $CpV(CO)_3$ is closely related to that produced in the photochemical synthesis reported here. However, its conversion to $Cp_2V_2(CO)_5$ in the original synthesis cannot involve attack on $CpV(CO)_4$ since it is not present under those conditions; high reactivity of $CpV(CO)_3$ toward species present in that synthesis ($CpV(CO)_3H^-$, $CpV(CO)_3$, etc.) is thus indicated.

The variable-temperature infrared studies reported here demonstrate the thermal instability of $CpV(CO)_3(THF)$. In contrast, irradiation of $CpNb(CO)_4$ in THF at 25 °C produces[14] $CpNb(CO)_3(THF)$, which is thermally stable in THF at 25 °C. The compounds $CpM(CO)_2(THF)$ (M = Mn, Re) exhibit a similar trend; the former is thermally unstable toward complete decarbonylation at 25 °C while the latter is quite stable.[14] The dimer synthesis reported here is unusual in that it proceeds by two sequential photochemical reactions. This attests to the kinetically inert character of $CpV(CO)_4$. By way of contrast,[15] $CpCo(CO)_2$ condenses readily with the photoproduct CpCoCO to produce $Cp_2Co_2(CO)_3$.

The thermal reaction of $CpV(CO)_4$ with phosphines in decalin proceeds by a dissociative mechanism. The ΔH^* value,[16] 55 kcal/mol, is one of the largest yet measured. The reaction occurs at a perceptible rate above 100 °C only because of a large positive ΔS^*, +36 eu. The observed ΔH^* value indicates that the unsaturated fragment $CpV(CO)_3$ is a very high-energy species. We have employed Cp_2V in an attempt to scavenge any CO librated by $CpV(CO)_4$. After 1 day in hexane solution at 25 °C, no Cp_2VCO was detected. After 4 days, trace quantities of Cp_2VCO are barely detectable by IR spectroscopy.

Thermal Reactivity of $Cp_2V_2(CO)_5$. Several mechanisms operate in the thermal reaction of Lewis bases with $Cp_2V_2(CO)_5$; the actual mechanism depends on the characteristics of the particular base. Weak nucleophiles (CO, PPh_3, dpm, THF) are unable to attack the pentacarbonyl dimer itself but instead react with $Cp_2V_2(CO)_4$, a species in equilibrium with the pentacarbonyl. This molecule bears a formal similarity to the highly reactive $Cp_2M_2(CO)_4$ species of the chromium group.[9] However, in contrast to the "double addition" of L to these dimers, the kinetic product of reaction of L with the divanadium tetracarbonyl has captured only a single L ($Cp_2V_2(CO)_4L$); the overall thermal reaction of weak nu-

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[12] In what follows, it is important to note that the carbonyl vibrational frequencies and intensities undergo no marked alteration on passing from hexane to THF.

[13] Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902.

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[15] Vollhardt, K.; Bercaw, J. E.; Bergman, R. G. *J. Organomet. Chem.* **1975**, *97*, 283.

[16] Faber, G. C.; Angelici, R. J. *Inorg. Chem.* **1970**, *9*, 1586.

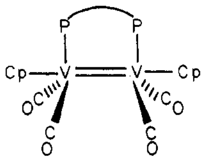
cleophiles with $Cp_2V_2(CO)_5$ is thus CO substitution, not addition.

Stronger nucleophiles such as PEt_2Ph are able to directly attack $Cp_2V_2(CO)_5$ (eq 4). This may be followed (Scheme II, eq 8) by direct displacement of the metal–metal double bond (eq 13). This mechanism, analogous to the triple-to-single metal–metal bond conversion observed on addition to $Cp_2Mo_2(CO)_4$, would imply that the V=V double bond is responsible for the enhanced reactivity of $Cp_2V_2(CO)_5$. The 16-electron fragments shown in eq 13 would be stabilized by coordination of THF (this reaction is observed to be faster in THF than in hexane). Alternatively, this reaction could take place through an intermediate, the phosphine adduct $Cp_2V_2(CO)_5(PEt_2Ph)$. Such a reaction requires internal displacement of carbonyl semibridges producing, for example, saturated species VI. Independent of this aspect of the mechanism, it is noteworthy that this associative path ultimately *displaces* the second metal center, producing monomers. We have neither spectroscopically detected nor isolated a simple addition product of formula $Cp_2V_2(CO)_5L$. In an attempt to promote formation of a species coordinating six two-electron donor ligands, we examined the reaction of $Cp_2V_2(CO)_5$ with $Ph_2PCH_2PPh_2$ (dpm). The idea here was to constrain a soft base in close proximity to the dimer in order to maximize the opportunity for addition. Irradiation of a saturated THF solution of $Cp_2V_2(CO)_5$ with equimolar dpm results in rapid appearance of a compound with four CO frequencies, the values of which are nearly identical with those of $Cp_2V_2(CO)_4(PPh_3)$. $CpV(CO)_3(dpm)$ also appears as a minor product and was independently shown to be a product of secondary photolysis of $Cp_2V_2(CO)_4(dpm)$. In THF solution at 25 °C, $Cp_2V_2(CO)_4(dpm)$ reacts further to form $CpV(CO)_3(dpm)$ as the only carbonyl-containing product.

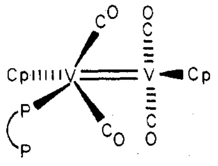
$$Cp_2V_2(CO)_5 + PEt_2Ph \rightarrow CpV(CO)_3 + CpV(CO)_2(PEt_2Ph) \quad (13)$$

$$\underset{\text{VI}}{Cp(CO)_3V{=}V(CO)_2(PEt_2Ph)Cp}$$

The dimer $Cp_2V_2(CO)_4(dpm)$ was characterized by infrared, mass, and proton NMR spectroscopy. The proton NMR of this dimer closely resembles that of $Cp_2V_2(CO)_4(PPh_3)$ and establishes the dpm dimer to be asymmetric with a monodentate chelate (VIII) rather than symmetric (VII). This is evident not only from the inequivalent Cp rings but also from the doublet peak due to the dpm methylene protons. This doublet is consistent with a P–H coupling constant which is distinctly larger when phosphorus is coordinated than when it is free; this behavior has been widely observed. Rapid intramolecular rearrangement involving P–V bond breaking and making is also excluded by these results.



VII



VIII

In order to properly evaluate the thermal reactivity of $Cp_2V_2(CO)_5$, it is useful to have a qualitative indication of the rate of thermal substitution of a reactive phosphine with $CpV(CO)_4$. This comparison, using PEt_2Ph, shows that reaction of the dimer is complete at a time when less than 3% of $CpV(CO)_4$ has reacted. The vanadium dimer, therefore, possesses the enhanced reactivity essential for efficient catalytic reactivity. The reaction of $Cp_2V_2(CO)_5$ with PEt_2Ph is not "instantaneous", however, as are addition reactions to authentic 16-electron species and to $Cp_2Mo_2(CO)_4$. The vanadium dimer is characterized by intermediate reactivity such as might be anticipated for a saturated complex (II) which can readily isomerize to an unbridged unsaturated form, either in isolation (V) or in response to the approach of the base. We feel that the complete set of observations reported here indicates that $Cp_2V_2(CO)_5$ should be considered as a saturated complex by virtue of donor semibridging carbonyl ligands. Such internal stabilization is weak in the sense that $Cp_2V_2(CO)_5$ exhibits greatly enhanced thermal reactivity toward all nucleophiles (compared to $CpV(CO)_4$); the dimer is best considered to be a lightly stabilized reactive species whose latent unsaturation can be revealed by using basic phosphines. In addition, the existence of a dissociative equilibrium producing $Cp_2V_2(CO)_4$ makes the dimer reactive toward even weak nucleophiles.[17]

Photochemical Reactivity of $Cp_2V_2(CO)$. The photochemical reactivity of $Cp_2V_2(CO)_5$ gives no indication of dimer scission, even under conditions (THF solvent) designed to stabilize $CpV(CO)_n$ (n = 2, 3) fragments. Similarly, irradiation in the presence of a chelate ligand (dpm), which would trap such fragments, gives no evidence for their formation. All of the results reported here are consistent with the primary photoprocess (more properly the primary chemical consequence of irradiation) being CO extrusion. The formation of substitution products of the intact dimer on irradiation is consistent with this, particularly in the case of PEt_2Ph. Here, it is possible to show that $Cp_2V_2(CO)_4(PEt_2Ph)$ does not react with further PEt_2Ph upon irradiation and that irradiation of $CpV(CO)_3(PEt_2Ph)$ produces no $Cp_2V_2(CO)_4(PEt_2Ph)$. Finally, unequivocal proof that the chemical consequence of light absorption by $Cp_2V_2(CO)_5$ is CO dissociation is provided by direct observation of $Cp_2V_2(CO)_4(THF)$ at −78 °C. These observations, therefore, support the argument, advanced above, that some multiple metal–metal bonds are stable to one-electron excitation. The particular utility of this result is that it offers the possibility for carrying out, as needed, substitution or addition reactions on multiply bonded oligomeric metal complexes; the potential for catalyst modification is clear.

To date, the photochemistry of organometallic compounds with cyclopentadienyl, carbonyl, and even alkyl ligands has generally resulted in duplication, at 25 °C, of the reactivity observed thermally under more vigorous conditions. This is the case for Lewis base dissociation, metal–metal bond homolysis, and alkane elimination. In the reaction of $Cp_2V_2(CO)_5$ with PEt_2Ph we have a clear example of disparate thermal chemistry and photochemistry. While photoacceleration of an observable thermal reaction is certainly useful, the possibility that irradiation will reveal reactivity quite distinct from that observed thermally immensely broadens the potential of photochemistry as a synthetic and catalytic technique. Those molecular characteristics which give rise to independent thermal and photochemical energy surfaces remain to be determined.[18]

Acknowledgment. This work was supported by the National Science Foundation (Grant No. CHE 77-10059). G. L. Hillhouse provided valuable technical assistance. We also are indebted to Professor D. J. Darensbourg, Tulane University,

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(17) Such a dissociative reaction is characteristic of a saturated species and is contrary to the behavior expected of a 16-electron complex (III).

(18) After this manuscript had been submitted a report appeared on the mechanism of the photochemical conversion of PR_3 and $Cp_2Fe_2(CO)_4$ to $Cp_2Fe_2(CO)_3PR_3$ (R = Ph, O-*i*-Pr).[19] An intermediate *adduct*, $Cp_2Fe_2(CO)_4PR_3$, in which the Fe–Fe bond has apparently been cleaved, was detected at −78 °C. We consider this mechanism to be less likely than CO dissociation for $Cp_2V_2(CO)_5$ since no such intermediate (e.g., $Cp_2V_2(CO)_5(THF)$) is detectable at −78 °C. If such an adduct is formed in our system, the energy minimum is not deep enough to allow differentiation from a transition state.

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for providing the quantitative vibrational analysis of $Cp_2V_2(CO)_5$ isotopomers using his least-squares program.

Registry No. $Cp_2V_2(CO)_5$, 41699-43-8; $CpV(CO)_4$, 12108-04-2; $Cp_2V_2(CO)_4PPh_3$, 68875-54-7; $CpV(CO)_3PPh_3$, 12213-09-1; $Cp_2V_2(CO)_4(dpm)$, 73557-86-5; $CpV(CO)_3(dpm)$, 73574-37-5; $CpV(CO)_2(dpm)$, 61818-84-6; $CpV(CO)_3(dppe)$, 73557-87-6; $CpV(CO)_2(dppe)$, 12304-19-7; $CpV(CO)_3(PEt_2Ph)$, 12184-66-6; *cis*-$CpV(CO)_2(PEt_2Ph)_2$, 73610-20-5; $Cp_2V_2(CO)_4(PEt_2Ph)$, 73557-88-7; $Cp_2V_2(CO)_4(THF)$, 73557-89-8; $CpV(CO)_3(THF)$, 73557-90-1.

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Comparative Studies of Hydridorhodoxime and Its Conjugate Base, Bis(dimethylglyoximato)rhodate(1−) Ion

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Various reactions of the title compounds have been studied, with determinations of products, stoichiometry, and kinetics in aqueous methanol. Hydridorhodoxime, $HRh(dmgH)_2P(C_6H_5)_3$, has $pK_a \approx 9.5$. A study of the forward and reverse rates of neutralization reveals three pathways corresponding to reactions of the rhodium(I) anion with H_3O^+, H_2O, and Tham buffer. Hydridorhodoxime is further protonated at the oxime oxygens in acidic solution and decomposes under these conditions to hydrogen and the dimeric Rh(II) derivative $[Rh(dmgH)_2P(C_6H_5)_3]_2$. Both title compounds react with organic halides, the base in an S_N2 reaction to form alkyl and aralkyl organorhodoximes and the acid by hydrogen transfer forming the hydrocarbon. The rate constants (k, $M^{-1}\ s^{-1}$) in the former reactions are 1.66×10^4 (benzyl bromide), 1.04×10^3 (benzyl chloride), 9.6×10 (1-phenylethyl chloride), and 5.2×10^{-1} (n-butyl bromide); the respective values for hydridorhodoxime are 9.6×10^2, 5.4×10, and 1.8×10 $M^{-1}\ s^{-1}$ (with n-butyl bromide not determined, owing to interference from decomposition). Various competition kinetic experiments were also performed to confirm the processes being studied. Reaction mechanisms are presented to account for the results obtained.

Introduction

The study of the catalytic properties of transition-metal–hydride complexes is a field of growing interest[1–5] in which there is a continuing need for quantitative data on the mode of M–H bond breaking and on the mechanism of hydrogen-transfer reactions. We set out to explore a number of quantitative issues relating to bis(dimethylglyoximato) complexes. Considering the cobalt complexes (so-called "cobaloximes"),[6] one recognizes that $HCo(dmgH)_2B$ and $Co(dmgH)_2B^-$ are related as conjugate acid and base.[7] Hydridocobaloxime[8] is, however, unstable toward hydrogen evolution:

$$2HCo(dmgH)_2B = H_2 + 2Co(dmgH)_2B \qquad (1)$$

This reaction is of interest in its own right[9] but interferes with a quantitative study of some of the chemistry underlying these compounds, such as the acid–base neutralization reactions and the role of the hydrido complex as a hydrogen-transfer reagent.

On the other hand there are several reports of the relatively higher kinetic stability of the rhodium–hydrogen bond as compared to the cobalt–hydrogen bond.[10,11] It has also been experimentally demonstrated that hydridorhodoximes such as $HRh(dmgH)_2P(C_6H_5)_3$ have catalytic properties in hydrogenation and hydrosilylation reactions.[12,13] Thus we have now investigated the formation and decomposition reactions of $HRh(dmgH)_2P(C_6H_5)_3$. In addition the reactions of alkyl halides with hydridorhodoxime and comparisons with the already reported[14] alkylation reactions of the conjugate base, $Rh(dmgH)_2P(C_6H_5)_3^-$, are of considerable interest. We have hence studied the reactions of benzyl chloride and bromide, α-phenylethyl chloride, and n-butyl bromide with $Rh(dmgH)_2P(C_6H_5)_3^-$ and $HRh(dmgH)_2P(C_6H_5)_3$ in aqueous methanolic (1:1) medium. Comparisons of the relative reactivities and the nature of products formed in these reactions have been made.

Experimental Section

Materials. Doubly distilled benzyl chloride, n-butyl bromide, 4-bromobenzyl bromide and 4-bromotoluene were used. Chloro(triphenylphosphino)bis(dimethylglyoximato)rhodium(III), $ClRh(dmgH)_2P(C_6H_5)_3$, was prepared by standard methods;[15] its purity was established by satisfactory elemental analyses and by the ^1H NMR spectrum. Anal. Calcd: C, 49.50; H, 4.63; N, 8.88. Found: C, 49.55; H, 4.62; N, 8.78.

(Triphenylphosphino)bis(dimethylglyoximato)rhodium(III) hydride, $HRh(dmgH)_2P(C_6H_5)_3$, was prepared by an adaptation of a published procedure.[16] Since it was found that rigorously oxygen-free conditions

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(7) The complex $Co(dmgH)_2B^-$ is clearly a derivative of univalent cobalt. Accepted conventions designate $HCo(dmgH)_2B$ as a derivative of cobalt(III) and (formally) the H^- ion, much like the analogues $ClCo(dmgH)_2B$ and $CH_3Co(dmgH)_2B$.

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