not possible for reactions of this complex, and an I_d mechanism was assigned.[22]

Although it is not clear why reaction of $P(OPh)_3$ should be so slow (or why that of $SbPh_3$ should be so fast), a consistent interpretation of the data would be to conclude that these same five ligands react with $(OC)_4\overline{Fe(\mu\text{-}AsMe_2)Co}(CO)_3$ by a concerted but largely dissociative I_d mechanism. The values of k_2 increase systematically along the series of increasingly basic ligands PPh_2Et, $PPhEt_2$, and P-*n*-Bu_3 to an extent compatible with increasing amounts of Co–P bond making and increasing I_a character.

The activation parameters in Table III show that $\Delta H_2^{\ddagger}$ decreases along the series $P(OPh)_3 > PPh_3 >$ P-*n*-$Bu_3 > P(C_6H_{11})_3$ in accordance with increasing Co–P bond making. The low value of k_2 for $P(C_6H_{11})_3$ compared with P-*n*-Bu_3 is due to a more unfavorable value of $\Delta S_2^{\ddagger}$, $\Delta H_2^{\ddagger}$ being slightly more favorable. This suggests that the steric effect may be due to a more limited path of approach for the nucleophile rather than a diminished degree of bond making. The values of $\Delta H_2^{\ddagger}$ for $AsPh_3$ and $SbPh_3$ are both fairly close to that for $P(OPh)_3$ and are higher than that for PPh_3. The unexpectedly high value of k_2 for $SbPh_3$ is due to an exceptional value of $\Delta S_2^{\ddagger}$, though whether this will turn out to be generally true remains to be seen.

We can conclude that the heterolytic Fe→Co bond-breaking reactions studied here are induced by a concerted but largely I_d bimolecular process for the less nucleophilic ligands. As the nucleophilic character of the ligands increases, there is an increasing degree of bond making in the transition state and the I_a character of the reaction with P-*n*-Bu_3 is probably quite large. No kinetic evidence is obtained for the formation of any coordinatively unsaturated intermediates during the reactions, and no estimates can be made from the kinetic parameters of the strengths of the Fe→Co bonds.

Acknowledgment. We thank Erindale College and the Natural Sciences and Engineering Research Council (NSERC), Ottawa, for support of this work. R.A.J. thanks the NSERC for the award of a research fellowship (1974–1977). We also thank NATO for a travel grant allowing collaboration with Professor Dr. H. Vahrenhamp of the University of Freiburg, Freiburg, West Germany. We also thank a reviewer for a helpful suggestion.

Registry No. $(OC)_4\overline{Fe(\mu\text{-}AsMe_2)Co}(CO)_3$, 50388-37-9; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(P(C_6H_{11})_3)$, 76402-85-2; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3$(P-*n*-$Bu_3$), 76402-86-3; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(PPhEt_2)$, 76402-87-4; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(PPh_2Et)$, 76402-88-5; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(P(OMe)_3)$, 54766-35-7; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(PPh_3)$, 54790-06-6; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(etpb)$, 76402-89-6; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(P(OPh)_3)$, 76402-90-9; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(AsPh_3)$, 76402-91-0; $(OC)_4Fe(\mu\text{-}AsMe_2)Co(CO)_3(SbPh_3)$, 76402-92-1; $P(C_6H_{11})_3$, 2622-14-2; P-*n*-Bu_3, 998-40-3; $PPhEt_2$, 1605-53-4; PPh_2Et, 607-01-2; $P(OMe)_3$, 121-45-9; PPh_3, 603-35-0; etpb, 824-11-3; $P(OPh)_3$, 101-02-0; $AsPh_3$, 603-32-7; $SbPh_3$, 603-36-1.

Supplementary Material Available: Table IV, a listing of observed pseudo-first-order rate constants (4 pages). Ordering information is given on any current masthead page.

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Photochemistry of Tetracarbonylbis(cyclopentadienyl)dichromium(I) and Related Compounds: Labilization of Carbon Monoxide

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Photochemistry of three related compounds, $(\eta\text{-}C_5H_5)_2Cr_2(CO)_4$, $(\eta\text{-}C_5Me_5)_2Cr_2(CO)_4$, and $(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)Cr_2CO)_4$, having a chromium–chromium triple bond has been examined, and the principal result is that the CO ligands are labilized by photoexcitation. Spectroscopically, the complexes are similar and exhibit a visible absorption at ~600 nm ($\epsilon \approx 300$ M^{-1} cm^{-1}) and a near-ultraviolet absorption at ~400 nm ($\epsilon \approx 10^4$ M^{-1} cm^{-1}) in alkane solution. Homolytic scission of the metal–metal triple bond is ruled out as a primary photoprocess by the facts that (i) irradiation of $(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)Cr_2(CO)_4$ in alkane solution does not yield $(\eta\text{-}C_5H_5)_2Cr_2(CO)_4$ and $(\eta\text{-}C_5Me_5)_2Cr_2(CO)_4$ and (ii) irradiation of both $(\eta\text{-}C_5H_5)_2Cr_2(CO)_4$ and $(\eta\text{-}C_5Me_5)_2Cr_2(CO)_4$ as a 1/1 mixture in alkane solution does not yield $(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)Cr_2(CO)_4$. Labilization of CO upon photoexcitation is established by irradiation of $(\eta\text{-}C_5H_5)_2Cr_2(CO)_4$ or $(\eta\text{-}C_5Me_5)_2Cr_2(CO)_4$ in alkane solution under a ^{13}CO (90% ^{13}C, 10% ^{12}C) atmosphere. Quantum yields for CO exchange are generally low and dependent on the excitation wavelength. The quantum yields for CO exchange for $(\eta\text{-}C_5Me_5)_2Cr_2(CO)_4$ are $<2 \times 10^{-4}$ at 633 nm, $(1.2 \pm 0.3) \times 10^{-3}$ at 458 nm, and $(4.0 \pm 1.0) \times 10^{-2}$ at 366 nm. The wavelength dependence is consistent with dissociative loss of CO from an upper excited state. When the complexes are irradiated in degassed alkane solution (in the absence of CO), decomposition occurs with an initial quantum yield similar to that for CO exchange. The presence of CO generally suppresses decomposition but not completely. The $(\eta\text{-}C_5Me_5)_2Cr_2(CO)_4$ is the least susceptible to decomposition in the presence of CO.

Introduction

Numerous studies of transition-metal compounds containing single metal–metal bonds have demonstrated that such bonds are subject to photochemical, homolytic scission in nonpolar solvents.[1] However, comparatively few investigations have addressed the question of the photochemical cleavage of metal–metal bonds whose order exceeds 1.[2] Geoffroy, Gray, and Hammond found that photolysis of $Re_2Cl_8^{2-}$, a complex with a quadruple Re$\overset{4}{-}$Re bond,[3] in acetonitrile leads to mononuclear *trans*-$[ReCl_4(NCCH_3)_2]^-$.[4a] However, subsequent flash-photolysis studies established that the Re$\overset{4}{-}$Re bond

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0020-1669/81/1320-1133\$01.25/0

Table I. Spectral Features of Dinuclear Cr Complexes[a]

complex	UV-vis, nm (ϵ, M^{-1} cm^{-1})[b]	IR, cm^{-1} (ϵ, M^{-1} cm^{-1})[c]
$(\eta\text{-}C_5H_5)_2Cr_2(CO)_6$	604 (270), 448 (5000), ~370 (sh)	2020 (4900), 1955 (4300), 1928 (4100), 1914 (4900), 1892 (2760)
$(\eta\text{-}C_5H_5)_2Cr_2(CO)_4$ (1)	625 (240), 391 (7100), 291 (11 500)	1909 (6700), 1886 (8400)
$(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)Cr_2(CO)_4$ (3)	614 (280), 397 (10 200), ~285 (sh)	1893 (7100), 1872 (8500)
$(\eta\text{-}C_5Me_5)_2Cr_2(CO)_4$ (2)	604 (300), 403 (12 700), 300 (11 300)	1878 (6800), 1858 (8000)
$(\eta\text{-}C_5Me_5)_2Cr_2(^{13}CO)_4$ (4) (90% ^{13}CO)	604 (340), 402 (14 300), 300 (12 400)	1845 (sh), 1835 (5400), 1815 (6600)

[a] All data for isooctane solutions at 298 K. [b] Band maxima in ±2 nm; ϵ ± 10%. [c] Band maxima in ±1 cm^{-1}; ϵ ± 10%.

cleavage probably results from CH_3CN attack of the electronic excited state of the dimer.[4b]

With the hope of observing dissociative cleavage of a multiple metal–metal bond, we have examined the photochemistry of the dinuclear chromium(I) compounds, $(\eta\text{-}C_5R_5)_2Cr_2(CO)_4$ (1, R = H; 2, R = Me) in hydrocarbon solvents. The observed diamagnetism of these compounds and application of the effective atomic number rule have led to the postulation of a triple Cr≡Cr bond in 1 and 2.[5,6] X-ray crystallographic studies of 1 and 2 reveal very short Cr≡Cr distances (2.20–2.23[7] and 2.28[8] Å, respectively) when compared with the Cr—Cr single-bond distance in $(\eta\text{-}C_5H_5)_2Cr_2(CO)_6$ (3.28 Å[9]).[10,11] In any case, the short Cr—Cr distance in 1 and 2 suggests a stronger Cr—Cr bond than in $(\eta\text{-}C_5H_5)_2Cr_2(CO)_6$. The value of the bond dissociation energy of 1 and 2 is not known, but obviously if the excitation energy does not exceed the energy to dissociate the molecule, the homolytic scission reaction will not occur. Formulating the Cr–Cr bond as a triple bond, one σ and two π bonds,[11] raises the additional concern that a one-electron excitation may not be sufficient to destroy the bond to a degree necessary to achieve dissociation. It is worth noting that the related complex $(\eta\text{-}C_5H_5)_2V_2(CO)_5$, which can be formulated as having a V═V bond, undergoes loss of CO, not V═V bond scission, as the primary photoreaction.[12]

An intriguing aspect of the tetracarbonyl dimers relates to the mechanism of their formation. Ginley, Bock, and Wrighton suggested that 1 is formed by the coupling of two 15-electron $(\eta\text{-}C_5H_5)Cr(CO)_2$ fragments, which are generated by thermal labilization of 17-electron $(\eta\text{-}C_5H_5)Cr(CO)_3$ species.[13] Microscopic reversibility requires that the reverse reaction, scission of the metal–metal bond to yield 15-electron fragments, be a viable reaction pathway. We report a series of ^{13}CO-exchange and attempted cross-coupling experiments with 1 and 2 to determine whether such a cleavage can be induced photochemically. A photochemical route to completely ^{13}CO-exchanged 2 and a thermal preparation of a new, mixed dimer, $(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)Cr_2(CO)_4$ (3), are also described.

Experimental Section

Spectra. Infrared spectra were recorded on a Perkin-Elmer 180 grating spectrometer. ^1H NMR spectra (60 MHz) were acquired on a Varian T-60 spectrometer and are reported in ppm with reference to a Me_4Si internal standard. ^{13}C NMR spectra were obtained at 25 MHz in the pulsed Fourier-transform mode on a JEOL FX-90Q. Data are reported in ppm with reference to Me_4Si. UV-visible absorption spectra were recorded on a Cary 17 spectrophotometer. Low-temperature spectra were obtained with use of an all-quartz liquid-N_2 Dewar fitted with optical quality quartz flats as windows. Mass spectra were obtained on a Varian MAT 122 mass spectrometer.

General Procedures. All synthetic operations were performed with use of standard Schlenk techniques under an N_2 or Ar atmosphere with dry, deoxygenated solvents. Photochemical reactions were carried out either under vacuum or under an N_2, Ar, or CO atmosphere in dry (distilled from CaH_2), deoxygenated, Spectrograde isooctane or C_6D_6.

Materials. Chromium hexacarbonyl was purchased from Pressure Chemical Co. and was used without further purification. Enriched ^{13}CO (90%) was purchased from Merck Sharp and Dohme. Pentamethylcyclopentadiene,[14] $(\eta\text{-}C_5H_5)_2Cr_2(CO)_4$ (1),[5] $(\eta\text{-}C_5Me_5)_2Cr_2(CO)_4$ (2),[15] $(\eta\text{-}C_5H_5)Cr(CO)_3I$,[5] and $Na[(\eta\text{-}C_5Me_5)Cr(CO)_3]$[16] were prepared according to the literature procedures.

Synthesis of $(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)Cr_2(CO)_4$ (3). Tetrahydrofuran (100 mL) was added through a cannula to a mixture of solid $Na[(\eta\text{-}C_5Me_5)Cr(CO)_3]$ (1.0 g, 3.4 mmol) and $(\eta\text{-}C_5H_5)Cr(CO)_3I$ (1.1 g, 3.3 mmol). Both solids dissolved rapidly to yield an air-sensitive red solution that was magnetically stirred for 1 h. Solvent was removed in vacuo, and *m*-xylene (100 mL) was added through a cannula. The mixture was refluxed for 4 h to a dark green color and then cooled to room temperature and filtered. Solvent was removed under reduced pressure, affording a dark green, microcrystalline solid (1.0 g, 70%), whose infrared and NMR spectra suggested a mixture of 1, 2, and 3. So that pure 3 could be isolated, the crude material was extracted into hot hexane (70 mL). The green solution was cooled (−30 °C, 24 h) and then filtered to give crystalline 2 (0.28 g) and a solution containing 3 with a trace of 2. Hexane was removed in vacuo from this solution, and the resulting solid was sublimed (10^{-5} torr, 75 °C) and crystallized from hexane (4 mL, −30 °C) to give mainly 3 (0.15 g, 10% yield). Only a small impurity (<10%) of 2 was detectable.

^1H NMR spectrum (60 MHz, C_6D_6): δ 1.63 (s, 2.8 H), 4.26 (s, 1 H). IR spectrum (isooctane solution): ν(CO) 1893 (ϵ 7090 M^{-1} cm^{-1}), 1872 cm^{-1} (ϵ 8850 M^{-1} cm^{-1}). IR spectrum (KBr pellet): 3110 (w), 2960 (w), 2920 (m), 2860 (w), 1940 (m), 1870 (vs), 1850 (vs), 1485 (w), 1425 (m), 1385 (s), 1350 (sh), 1115 (w), 1072 (w), 1028 (m), 840 (w), 820 (m), 630 (m), 550 (s), 455 (m), 415 (w), 385 (w) cm^{-1}. The mass spectrum of 3 exhibits isotopic clusters about the masses [ion, *m/e* (relative abundance)]:[17] P^+, 416 (0.69); $[P - CO]^+$, 388 (56.55); $[P - 2CO]^+$, 360 (1.70); $[P - 3CO]^+$, 332 (9.61); $[P - 4CO]^+$, 304 (33.23). Weak peaks due to 2 are also observed: P^+, 486 (0.13); $[P - CO]^+$, 485 (7.19); $[P - 2CO]^+$, 430 (0.08); $[P - 3CO]^+$ (2.18); $[P - 4CO]^+$, (4.32).

$(\eta\text{-}C_5Me_5)_2Cr_2(^{13}CO)_4$ (4). A solution of 2 (0.06 g, 0.12 mmol) in dry, deoxygenated isooctane (60 mL) was transferred with a syringe into a septum-capped 500-mL Pyrex flask containing ^{13}CO (90% isotopically enriched) at 1 atm (ca. 20 mmol ^{13}CO, 40-fold excess). The solution was irradiated with a GE Blacklite (355 ± 20 nm, two 15-W bulbs) for 24 h and then withdrawn with a syringe and transferred to an N_2-filled Schlenk tube. The solution was concentrated

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(10) The crystal structures of 1[7] and 2[8] reveal unusual semibridging carbonyls. Donation of electron density from metal orbitals to CO orbitals of π symmetry has been suggested.[11] The bridging CO's have also been suggested to be donors: Curtis, M. D.; Han, K. R.; Butler, W. M. *Inorg. Chem.* **1980**, *19*, 2096–2101. In either view the Cr≡Cr bond order is reduced from 3. Nonetheless, the short Cr—Cr bonds in 1 and 2 indicate a metal–metal bond order substantially greater than 1.

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(17) Only masses corresponding to $[(\eta\text{-}C_5R_5)_2Cr_2(CO)_n]^+$ species are reported. For 3, the relative abundance is based on the *m/e* 252 (100) peak; for 4, the *m/e* 372 (100) peak.

to ca. 7 mL (heated and then chilled −20 °C; 24 h) to give crystalline **4**. The mother liquor was decanted from the solid **4** with a cannula, and the solid was washed with ice-cold pentane (2 × 5 mL) and then dried in vacuo; yield 0.03 g (50%).

IR spectrum (KBr pellet): 2990 (w), 2960 (w), 2920 (m), 2860 (w), 1890 (m), 1830 (vs), 1810 (vs), 1482 (m), 1450 (m), 1422 (w), 1380 (ms), 1070 (w), 1030 (m), 620 (m), 560 (m), 535 (m), 495 (m), 450 (w), 420 (w), 399 (w) cm^{-1}. IR spectrum (isooctane solution): ν(CO) 1845 (sh), 1835 (ϵ = 5410 M^{-1} cm^{-1}), 1815 cm^{-1} (ϵ = 6640 M^{-1} cm^{-1}). For comparison, the IR spectrum of **2** in a KBr pellet exhibits absorptions at 2990 (w), 2980 (w), 2920 (m), 2860 (w), 1875 (vs), 1845 (vs), 1482 (m), 1450 (m), 1420 (w), 1380 (ms), 1070 (w), 1029 (m), 633 (m), 563 (m), 546 (ms), 506 (m), 461 (w), 417 (w), and 399 (w) cm^{-1}; the IR spectrum in isooctane solution exhibits ν(CO) 1878 (ϵ 6810 M^{-1} cm^{-1}) and 1858 cm^{-1} (ϵ 8000 M^{-1} cm^{-1}). For **4**, the ^{1}H NMR spectrum (60 MHz, C_6D_6) shows δ 1.73 (s). The same value is obtained for **2** in C_6D_6. The UV–visible spectrum of **4** in isooctane solution shows the following peaks (extinction coefficients, M^{-1} cm^{-1}): 604 nm (336); 402 nm (14 330); 300 nm (12 430). For comparison with **2**, see Table I.

The mass spectrum of **4** at 80 eV exhibits isotopic clusters about the masses [ion, *m/e* (relative abundance)]:[17] P^+, 490 (0.17); $[P - {}^{13}CO]^+$, 461 (19.40); $[P - 2{}^{13}CO]^+$, 432 (1.80); $[P - 3{}^{13}CO]^+$, 403 (10.61); $[P - 4{}^{13}CO]^+$, 374 (24.61). The ^{13}C NMR spectrum of **4** in C_6D_6 (0.6 mL of 0.1 M **4**) showed a very strong singlet at 251.2 ppm vs. Me_4Si after four transient acquisitions (90-s pulse delay).

Photolysis Procedures. Isooctane solutions of **1**–**3** and/or **4** were irradiated in Pyrex vessels with (i) a GE Blacklite (355 ± 20 nm), (ii) a filtered 450-W medium-pressure Hg arc lamp (313 and 366 nm), (iii) a Coherent Radiation Model 60-8H He/Ne laser (633 nm), or (iv) a Spectra Physics Model 164 argon ion laser (458 nm). An isooctane solution of **4** in isooctane in a Vycor tube was irradiated with a UV-Products low-pressure Hg lamp (254 nm). Irradiation intensities were monitored by ferrioxalate actinometry (313, 366 nm)[18] or with a Tektronix Model J16 digital photometer equipped with a Model J6502 probe. Quantum yield measurements were based on the disappearance of starting material infrared absorptions.

^{13}CO-exchange experiments were performed in an apparatus consisting of a septum-capped 40 × 1.5 cm tube connected by means of a three-way stopcock to a vacuum line and a break-seal 100-mL ampule of ^{13}CO gas (90% isotopically enriched). A solution of **1** or **2** in rigorously dried isooctane (ca. 30 mL; 10^{-3} M **1** or **2**) was introduced into the Ar-filled tube with a cannula and then was degassed by three freeze–pump–thaw cycles. The vessel was isolated from the vacuum pump, and the seal on the ^{13}CO ampule was broken with a steel bar inside the tube. The solution was warmed to room temperatue and then magnetically stirred for 1 h to allow gas equilibration. The tube was inserted between the bulbs of the GE Blacklite for irradiation. Aliquots of the solution were withdrawn periodically with a syringe for infrared analysis.

Results and Discussion

a. Electronic Spectra of Complexes. The Cr≡Cr triple-bonded complexes studied have very similar optical properties (Figure 1 and Table I). Each exhibits a low-energy (~600 nm; ϵ ~300 M^{-1} cm^{-1}) visible absorption and a shoulder on the low-energy side of a sharp, intense (ϵ ~10^4 M^{-1} cm^{-1}) near-UV absorption at ~400 nm. A UV absorption feature also appears at ~300 nm.

Jemmis, Pinhas, and Hoffmann[11] have recently considered the electronic structure of the $(\eta\text{-}C_5R_5)_2M_2(CO)_4$ complexes, and the qualitative molecular orbital diagram in Chart I seems appropriate. As can be seen, a number of one-electron transitions are possible and additionally charge-transfer transitions to and from the M_2 core are possible. Our aim here is to provide an assignment to the salient features of the optical spectrum to develop a framework for considering the excited-state chemistry.

We associate the prominent ~400-nm band with the $\sigma_b \rightarrow \sigma^*$ transition. This assignment is supported by a comparison with the Cr–Cr single-bonded complex $(\eta\text{-}C_5H_5)_2Cr_2(CO)_6$ (Figure 2) and with the corresponding Mo and W species.[19] $(\eta\text{-}C_5H_5)_2Cr_2(CO)_6$ exhibits an intense absorption in the visible region at 448 nm (ϵ ~5000 M^{-1} cm^{-1}) that can be attributed to the $\sigma_b \rightarrow \sigma^*$ transition found at ~390 and ~370 nm for

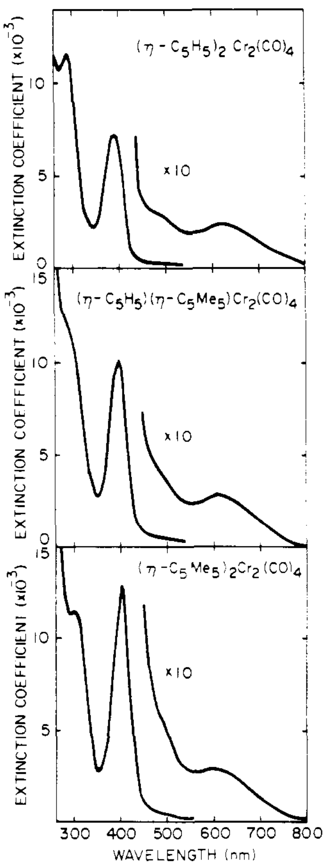
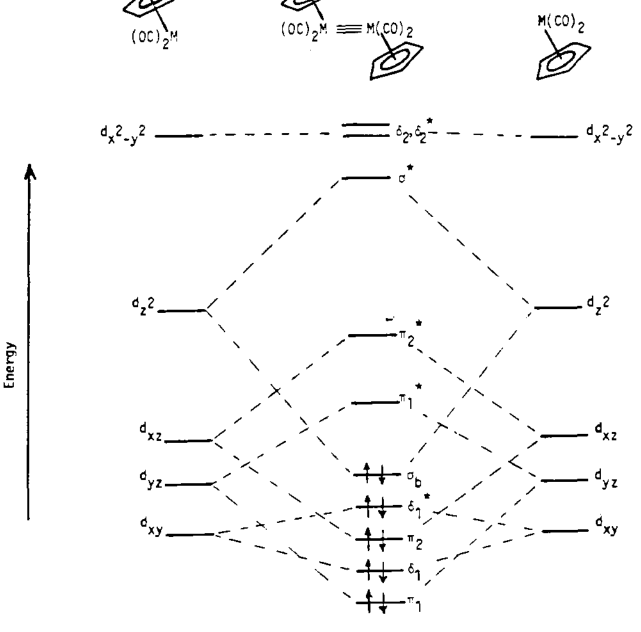


Figure 1. Optical absorption spectra of complexes in isooctane solvent at 298 K. Extinction coefficient is in units of M^{-1} cm^{-1}. Band maxima and absorptivities are listed in Table I.

Chart I. Qualitative Orbital Diagram for the d^5–d^5 $(\eta\text{-}C_5R_5)_2Cr_2(CO)_4$ Triple-Bonded Complexes Adapted from Ref 11



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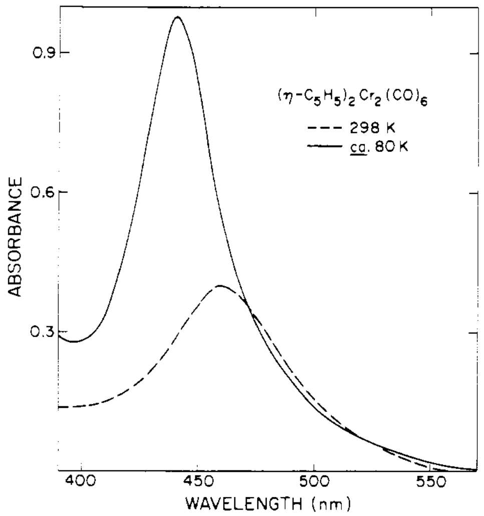

Figure 2. Optical absorption spectra of $(\eta\text{-}C_5H_5)_2Cr_2(CO)_6$ in 3-methylpentane at 298 K (---) and 77 K (—). The low-temperature spectrum has not been corrected for ~25% solvent contraction upon cooling from 298 to 77 K. See Table I for 298 K absorptivities.

the analogous Mo and W species,[19] respectively. The relatively low energy of the $\sigma_b \rightarrow \sigma^*$ absorption in the Cr complex may be due to the fact that the Cr–Cr single bond is significantly longer than would be expected, compared to the Mo and W species.[9] The decrease in the bond distance between the Cr atoms in the triple-bonded complex should result in a higher energy $\sigma_b \rightarrow \sigma^*$ excitation; the intense band at ~400 nm in $(\eta\text{-}C_5R_5)_2Cr_2(CO)_4$ would represent a blue shift of ~2500 cm^{-1} compared to the $\sigma_b \rightarrow \sigma^*$ energy in the $(\eta\text{-}C_5H_5)_2Cr_2(CO)_6$. There is also a large energy difference in the position of the intense near-UV band in $(\eta\text{-}C_5R_5)_2Mo_2(CO)_6$ (380–400 nm) and $(\eta\text{-}C_5R_5)_2Mo_2(CO)_4$ (~325 nm).[13] The relative position of the $\sigma_b \rightarrow \sigma^*$ absorption has been previously correlated with M–M bond distance in related complexes, and the energetic ordering of the $\sigma_b \rightarrow \sigma^*$ absorption is such that shorter bonds give a higher energy absorption.[20] Similarly, the energy of the $\delta \rightarrow \delta^*$ absorption in complexes exhibiting a $M\overset{4}{-}M$ quadruple bond can be correlated with the bond distance.[21]

The temperature dependence of M–M $\sigma_b \rightarrow \sigma^*$ absorptions is interesting.[22] Earlier studies on $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and their derivatives show that there is a temperature dependence such that the band sharpens, blue shifts, and intensifies somewhat as temperature is lowered. The temperature dependence of the intense ~480-nm band in $(\eta\text{-}C_5H_5)_2Cr_2(CO)_6$ thus accords well with the expectation for the $\sigma_b \rightarrow \sigma^*$ excitation (Figure 2). The larger than usual intensification may reflect the fact that $(\eta\text{-}C_5H_5)_2Cr_2(CO)_6$ is partially dissociated to $(\eta\text{-}C_5H_5)Cr(CO)_3$ in solution at 298 K.[9] The ~480-nm band also blue shifts to a greater degree than is usually encountered.[1,22] Since the effects of temperature on the $\sigma_b \rightarrow \sigma^*$ absorption have been attributed to the variable population of the vibrational levels of the M–M core, we might expect a large effect from temperature on the long Cr–Cr single-bonded complex. When the Cr–Cr bond is long, the higher vibrational levels of the Cr_2 core can be populated. The temperature dependence of $(\eta\text{-}C_5Me_5)_2Cr_2(CO)_4$ is shown in Figure 3 and does reveal intensification and a blue shift of the ~400-nm band. However, for this $Cr\equiv Cr$ triple-bonded species the shift is only ~300 cm^{-1} whereas the blue shift for the Cr—Cr single-bonded species is about 1000 cm^{-1}. The smaller shift for the triple-bonded species is consistent with a smaller 298 K population of the upper vibrational levels of the Cr_2 core when there is a multiple bond.

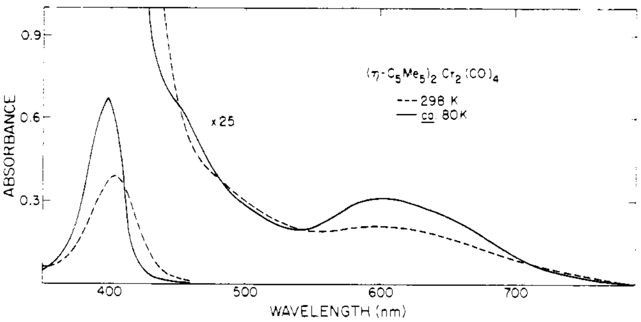

Figure 3. Optical absorption spectra of $(\eta\text{-}C_5Me_5)_2Cr_2(CO)_4$ in 3-methylpentane at 298 (---) and 77 K (—). The low-temperature spectrum has not been corrected for ~25% solvent contraction upon cooling from 298 to 77 K. See Table I for 298 K absorptivities.

The $Cr\equiv Cr$ bond distance has been measured for both $(\eta\text{-}C_5Me_5)_2Cr_2(CO)_4$ (2.28 Å)[8] and $(\eta\text{-}C_5H_5)_2Cr_2(CO)_4$ (2.20–2.23 Å).[7] The shorter $Cr\equiv Cr$ bonded complex has its $\sigma_b \rightarrow \sigma^*$ absorption at 391 nm (25 575 cm^{-1}) compared to 403 nm (24 814 cm^{-1}) for the longer $Cr\equiv Cr$ bonded system, consistent with the assignment of the ~400-nm band as the $\sigma_b \rightarrow \sigma^*$ absorption. The $(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)Cr_2(CO)_4$ complex, for which the $Cr\equiv Cr$ distance is not known, exhibits a band (397 nm, 25 189 cm^{-1}) between those found for the symmetrical complexes, and we therefore expect an intermediate $Cr\equiv Cr$ bond distance.

An alternative assignment for the ~400-nm absorption feature of the $Cr\equiv Cr$ bonded species is the $\pi_2 \rightarrow \pi_1^*$ transition. This would then suggest that the ~300-nm shoulder is the $\sigma_b \rightarrow \sigma^*$ absorption. The $\pi_2 \rightarrow \pi_1^*$ assignment to the ~400-nm feature cannot be ruled out on the basis of the data available now. Assigning the ~300-nm feature to the $\sigma_b \rightarrow \sigma^*$ transition would then give an ~10 000-cm^{-1} blue shift compared to the $\sigma_b \rightarrow \sigma^*$ absorption in the single-bonded $(\eta\text{-}C_5H_5)_2Cr_2(CO)_6$ complex. The ~10 000-cm^{-1} shift would in fact accord better with the rather large change in Cr–Cr distance in the single-bonded compared to that in the triple-bonded complexes. The $\pi_2 \rightarrow \pi_1^*$ absorption would be expected to vary in position with Cr–Cr distance and the ~800-cm^{-1} shift between $(\eta\text{-}C_5H_5)_2Cr_2(CO)_4$ and $(\eta\text{-}C_5Me_5)_2Cr_2(CO)_4$ would be a reasonable shift. Resolving the $\sigma_b \rightarrow \sigma^*$ vs. the $\pi_2 \rightarrow \pi_1^*$ assignment requires further investigation. For now, we note that either $\sigma_b \rightarrow \sigma^*$ or $\pi_2 \rightarrow \pi_1^*$ will weaken the $Cr\equiv Cr$ bond, and the photochemical experiments (vide infra) have been carried out with use of excitation wavelengths short enough to populate the $\sigma_b \rightarrow \sigma^*$ state even if the ~300-nm absorption feature corresponds to the $\sigma_b \rightarrow \sigma^*$ transition.

The first absorption band, at ~600 nm, is a relatively weak absorption and resembles the position and intensity of the first absorption (π–d $\rightarrow \sigma^*$) in mononuclear complexes such as $(\eta\text{-}C_5R_5)M(CO)_3X$ and in dinuclear, metal–metal single-bonded complexes such as $(\eta\text{-}C_5R_5)_2M_2(CO)_6$.[19] This band and the shoulder at ~500 nm are logically associated with less allowed transitions. At this time we are not in a position to make a definitive assignment in the triple-bonded complexes, but we suggest that the transition may be the $\delta_1^* \rightarrow \delta_2$ one. In one-electron terms, this is the only transition (see Chart I) that would have a larger excitation energy when the bond is stretched (cf. Table I for λ_{max} for C_5H_5 vs. C_5Me_5). However, the position of the first band could also be controlled by the changes in geometry and electron-donating properties associated with $\eta\text{-}C_5H_5$ vs. $\eta\text{-}C_5Me_5$. Detailed spectroscopic studies are required in order to resolve this issue, since the

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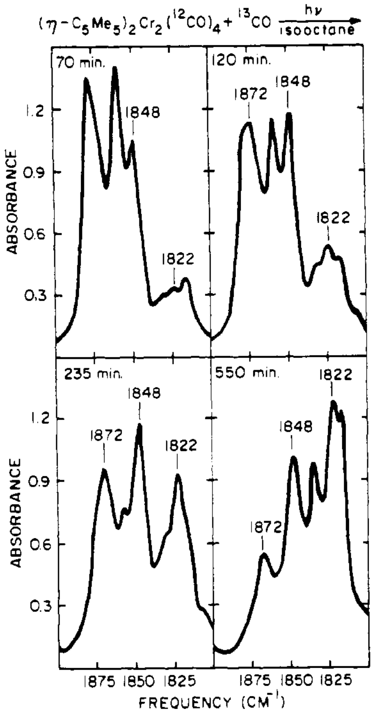

Figure 4. Infrared spectral changes (CO stretching region only) accompanying near-ultraviolet (355 ± 20 nm) irradiation of (η-$C_5Me_5)_2Cr_2(^{12}CO)_4$ in the presence of a 40-fold excess of ^{13}CO (90%-enriched) at 1 atm. The solvent is dry, deoxygenated isooctane. For spectra of starting complex and final complex see Figure 5.

changes in optical properties are modest and likely due to a combination of factors.

b. Attempted Photochemical Cross-Coupling Reactions. The lowest excited states of (η-$C_5R_5)_2Cr_2(CO)_4$ involve population of orbitals that can substantially weaken the Cr≡Cr triple bond. To test the possibility that light can be used to effect the reaction represented by eq 1, we have irradiated mixtures

$$(\eta\text{-}C_5R_5)_2Cr_2(CO)_4 \xrightarrow{h\nu} 2(\eta\text{-}C_5R_5)Cr(CO)_2 \qquad (1)$$

of **1** and **2** to determine whether **3**, the expected cross-coupling product, is formed. Near-UV irradiation (355 ± 20 nm) of a 1/1 mixture of **1** and **2** in isooctane solution results only in the decomposition of the two complexes; the infrared bands in the CO stretching region decline and no new metal carbonyl products are detectable. Complex **1** disappears more rapidly than **2**, and the decomposition can be suppressed under 1 atm of CO but still no new metal carbonyl products are detectable by infrared spectroscopy. In particular, we do not find that complex **3** forms from irradiation of **1** and **2** under any conditions that we have used. Even flash photolysis of a mixture of **1** and **2**, where the highest concentration of 15-e fragments could be generated, does not yield **3**. Irradiation of **3** likewise does not yield a mixture of **1** and **2**. Irradiation at 366, 313, or 254 nm or flash photolysis only leads to the decline of starting material, and no new metal carbonyl products are detectable. From the attempted cross-coupling experiments, we conclude that the complexes **1**–**3** are photosensitive, but the lack of cross-coupled products leads us to conclude that chemistry according to eq 1 is at best a small component of the excited-state decay paths.[23]

c. Photochemical CO Exchange. The ability to suppress photodecomposition of **1**–**3** by CO suggests that dissociative

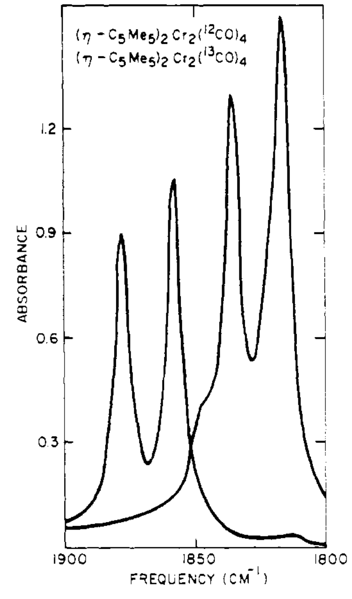

Figure 5. Infrared spectra of isooctane solutions of (η-$C_5Me_5)_2Cr_2(^{12}CO)_4$ (natural abundance) (1878, 1858 cm^{-1}) and (η-$C_5Me_5)_2Cr_2(^{13}CO)_4$ (90%-enriched) (1835, 1815 cm^{-1}). See Table I for extinction coefficients.

and reversible CO loss is the principal chemical result of photoexcitation (eq 2). In isooctane solution at 298 K, neither

$$(\eta\text{-}C_5R_5)_2Cr_2(CO)_4 \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} (\eta\text{-}C_5R_5)_2Cr_2(CO)_3 + CO \qquad (2)$$

1 nor **2** reacts thermally with ^{13}CO at 1 atm pressure. This is consistent with the earlier findings that the tetracarbonyl dimers react with CO to give the corresponding hexacarbonyl dimers—(η-$C_5R_5)_2Cr_2(CO)_6$ (R = H, Me)—only at CO pressures exceeding 100 atm.[13,15] However, ultraviolet irradiation of isooctane solutions of **1** or **2** under a ^{13}CO atmosphere results in infrared spectral changes that indicate the replacement of coordinated ^{12}CO by ^{13}CO. The significant features of these spectral changes in the case of **2** are illustrated in Figures 4 and 5, and may be summarized as follows. First, new absorption bands grow at 1872 and 1848 cm^{-1} at the expense of the starting material 1878- and 1858-cm^{-1} bands. Next, a new, 1822-cm^{-1} absorption grows in intensity while the 1872-cm^{-1} band diminishes. Finally, the 1848- and 1822-cm^{-1} bands decrease in intensity while two new absorptions at 1815 and 1835 cm^{-1} become predominant. No new features in the infrared spectrum are observed when photolysis is continued past this point. In accordance with the predicted Redlich-Teller isotope shift[24] ($\nu(^{13}CO) = 0.978\ \nu(^{12}CO) = 1818, 1837\ cm^{-1}$), the 1815- and 1835-$cm^{-1}$ absorptions are assigned to (η-$C_5Me_5)_2Cr_2(^{13}CO)_4$ (**4**). Independent spectroscopic and chemical evidence supports this structural assignment. The ^1H NMR and UV–vis spectra of **2** and **4** are essentially identical. With the exception of the carbonyl stretching frequencies, the infrared spectra of **2** and **4** are also virtually identical (some slight shifts in frequency are observed on infrared bands in the 600–200-cm^{-1} region). As has been found for **2**,[25] the mass spectrum of **4** exhibits $[(\eta\text{-}C_5Me_5)_2Cr_2(CO)_n]^+$, n = 0–4 ions, but in the case of **4**, the n = 4 peak occurs at m/e 490 rather than 486 and the n = 0 through n = 4 peaks are separated by integral multiples of 29 rather than 28. The ^{13}C NMR spectrum of **4** in C_6D_6 exhibits a single sharp resonance at 251.2 ppm after only four transient acquisitions.[26,27] This is in the region normally

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(23) We note that the triple-bonded complexes $Mo_2(NMe_2)_6$ and $W_2(NMe_2)_6$ do not undergo photoinduced cross-coupling either: Chisholm, M. H.; Extine, M. W.; Kelly, R. L.; Mills, W. C.; Murillo, C. A.; Rankel, L. A.; Reichert, W. W. *Inorg. Chem.* **1978**, *17*, 1673–1675.

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Table II. Quantum Yields for Reaction of Dinuclear Cr Complexes[a]

complex	reaction	quantum yield × 10^4 (±20%)			
		633 nm	458 nm	366 nm	313 nm
$(\eta\text{-}C_5Me_5)_2Cr_2(CO)_4$ (2)	disappearance	<2.8	15	140	800
	disappearance under 1 atm of CO			<7.5	140
	CO Exchange[b]	<2	12	400	
$(\eta\text{-}C_5H_5)_2Cr_2(CO)_4$ (1)	disappearance			200	640
	disappearance under 1 atm of CO			55	680
$(\eta\text{-}C_5H_5)(\eta\text{-}C_5Me_5)Cr_2(CO)_4$ (3)	disappearance			280	
	disappearance under CO			110	

[a] All data for isooctane solutions at 298 K. [b] Obtained by irradiating $(\eta\text{-}C_5Me)_2Cr_2(^{13}CO)_4$ (90% ^{13}C) in the presence of 1 atm natural-abundance ^{12}CO.

ascribed to metal carbonyl ^{13}C resonances. Finally, irradiation of **4** in isooctane (λ < 454 nm) under a ^{12}CO atmosphere regenerates **2**, as determined by infrared spectroscopy. The infrared spectral changes observed in the reversion of **4** to **2** are the reverse of those seen in the conversion of **2** into **4**. Ultraviolet-visible spectra of dilute ($<10^{-3}$ M) solutions of **2** before and after conversion to **4** show that the transformation proceeds in better than 90% spectroscopic yield. On a preparative scale (2×10^{-4} mol, **2**), a 50% isolated yield of **4** is realized.

The unalkylated tetracarbonyl dimer **1** also undergoes photochemical ^{13}CO exchange in isooctane solution. During the course of the transformation of **1** into the presumed $(\eta\text{-}C_5H_5)_2Cr_2(^{13}CO)_4$, the starting material 1909- and 1886-cm^{-1} bands diminish and new bands appear at 1903, 1879, and 1852 cm^{-1}. Finally, these absorptions decrease in relative intensity and two new features at 1864 and 1846 cm^{-1} predominate. In accordance with the expected isotope shift, these bands are assigned to $(\eta\text{-}C_5H_5)_2Cr_2(^{13}CO)_4$ (**5**) (predicted ν(CO) = 1866, 1846 cm^{-1}). Unfortunately, at ca. 1 atm ^{13}CO pressure, the photochemical ^{13}CO substitution in **1** is competitive with the photodegradation of **1** to intractable, non-carbonyl-containing products. Ultraviolet irradiation times required to completely convert **1** into **5** result in greater than 80% decomposition of the sample. Hence, the isolation of pure **5** does not prove practical.

We note that five $(\eta\text{-}C_5R_5)_2Cr_2(^{12}CO)_n(^{13}CO)_{4-n}$ (n = 1–3) species (including geometric isomers) are expected to form during the conversion of **2** into **4** or **1** into **5** if the substitution mechanism involves sequential exchange of coordinated ^{12}CO for ^{13}CO. A group-theoretical analysis shows that these five species could give rise to a total of 18 allowed infrared stretches. During the conversion of **1** into **5** and **2** into **4**, only three distinct intermediate infrared absorptions are resolved (vide supra). Changes in the relative intensities of these three bands with increased irradiation times indicate that the three bands are associated with three *separate compounds*. None of the $(\eta\text{-}C_5R_5)_2Cr_2(^{12}CO)_n(^{13}CO)_{4-n}$ (n = 1–3) species are expected to exhibit a single infrared-active stretch, so we assume that our failure to detect all of the 18 intermediate bands is due to either accidental degeneracy or instrumental limits of resolution.

Irradiation of an equimolar mixture of **2** and **4** in the absence of added CO results in the decline of the four infrared bands attributable to the two pure compounds. New infrared bands grow at 1872, 1848, and 1822 cm^{-1} and become the dominant features in the spectrum. These new absorptions occur at the same frequencies observed when **2** is irradiated under ^{13}CO or when **4** is irradiated under ^{12}CO (Figures 4 and 5). These results show that scrambling of CO between **2** and **4** can occur. The lack of cross-coupling products from irradiation of **1** and **2** or from **3** leads us to conclude that photochemical scrambling of CO between **2** and **4** proceeds via the primary photogeneration of the tricarbonyl species represented by eq 2 followed by statistical scavenging of the photoreleased ^{12}CO (from **2**) and ^{13}CO (from **4**).

Photodecomposition of **1**–**4** presumably originates with the loss of CO as in eq 2. The resulting species is expected to be very reactive, and trace quantities of H_2O, O_2, or other impurities may lead to its irreversible decomposition. Attempts to photochemically synthesize substitution products via irradiation of **1** or **2** in the presence of entering ligands such as ethylene, PPh_3, or $P(OMe)_3$ lead to significant decomposition. Irradiation of **2** in the presence of PF_3 does lead to substitution products but these have not been fully characterized.

d. Wavelength Dependence of Photoreaction Quantum Yields. Quantum yields for photodecomposition with and without a CO atmosphere are given in Table II. The quantum yields for disappearance of $(\eta\text{-}C_5Me_5)_2Cr_2(^{13}CO)_4$ in the presence of ^{12}CO are also given. The data show that irradiation corresponding to the position of the lowest energy absorption results in little or no reaction. As the irradiation wavelength is shifted into the UV, the reaction quantum yields increase significantly.

Referring to Chart I and the discussion of the absorption data (vide supra), the lowest excited states apparently do not result in a significant enough change in bonding to effect either loss of CO or complete cleavage of the Cr≡Cr triple bond within the lifetime of the excited state. Upper excited states involve population of the σ^* level, and this weakens both the Cr≡Cr bond and the Cr—CO bonds. Loss of CO is apparently very competitive with both Cr≡Cr bond cleavage and relaxation to the lower, unreactive excited states. Complexes containing M–M single bonds are typically efficiently cleaved by light that gives the $\sigma_b \rightarrow \sigma^*$ transition.[1,19] But though M–M bond cleavage dominates the photochemistry of species such as $(\eta\text{-}C_5H_5)_2M_2(CO)_6$ (M = Mo, W),[19] the $\sigma_b \rightarrow \sigma^*$ transition should significantly weaken M–CO bonds as well. Indeed, there is the possibility[28] of a low quantum efficiency formation of $(\eta\text{-}C_5H_5)_2Mo_2(CO)_5$ from $(\eta\text{-}C_5H_5)_2Mo_2(CO)_6$. Irradiation of $Co_2(CO)_8$ at low temperature results in loss of CO to give $Co_2(CO)_7$, evidencing lability of CO in the lowest excited states of M–M single-bonded complexes.[29] Interestingly, upper excited states were found to be more active than the lowest excited state. In the Cr≡Cr triple-bonded species, the two π bonds can apparently retard cleavage even upon $\sigma_b \rightarrow \sigma^*$ excitation and CO loss becomes the dominant photoreaction. Significantly lower quantum yields for M–M cleavage in single-bonded complexes have been observed upon excitation of lower energy transitions such as $\pi\text{–}d \rightarrow \sigma^*$, and thus the wavelength effects observed here are not unique.[19,30] Likewise

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(26) The ^{13}C NMR resonances normally associated with the $\eta\text{-}C_5Me_5$ ligand[27] at ca. 10 ppm (methyl carbon) and ca. 100 ppm (ring carbon) were not observed during this limited acquisition.

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the lowest excited state of $Re_2Cl_8^{2-}$ is unreactive.[4] Finally, the related metal carbonyl, $(\eta\text{-}C_5H_5)_2V_2(CO)_5$, having a V=V double bond appears to lose CO as the primary photoreaction; it is not known whether this is an upper excited-state process.[12]

Conclusions

We conclude that the excited states produced by >254-nm irradiation of $(\eta\text{-}C_5R_5)_2Cr_2(CO)_4$ do not reduce the $Cr\equiv Cr$ bond order sufficiently to allow dissociative $Cr\equiv Cr$ cleavage to compete with Cr—CO cleavage. Thus, we have been unable to photogenerate 15-e fragments from the $M\equiv M$ triple bonded species. Reactive $(\eta\text{-}C_5R_5)_2Cr_2(CO)_3$ fragments are produced with a quantum efficiency that is highest in the ultraviolet and does not exceed 10^{-1}. It is not known whether the excitation energies used actually exceed the $Cr\equiv Cr$ bond dissociation energy. Therefore, we cannot uneuivocally conclude that fast alternative decay channels (e.g., CO loss) prevent the $Cr\equiv Cr$ scission.

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Fluxionality and Basicity of $Cp_2Re_2(CO)_5$

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$(C_5H_4R)_2Re_2(CO)_5$ (R = H and Me) both exhibit rapid interchange of their three distinct CO environments at −83 °C. This proceeds by a nondissociative mechanism. Enantiomerization of the molecule is also demonstrated to occur in the same temperature range with use of ^1H and ^{13}C NMR. A transition state devoid of bridging carbonyls is proposed for this process. Both dimers are protonated ($HOSO_2CF_3$ at low temperatures) at the Re–Re bond to give a stereochemically rigid product. The $\nu(CO)$ value of the bridging carbonyls in the protonated and deprotonated forms are essentially identical; an explanation of this unusual result is proposed.

Introduction

The question of the site of protonation of dimeric and cluster metal carbonyl derivatives is a matter of longstanding interest. Protonations at a metal–metal bond[1,2] and at a carbonyl oxygen[3] are viable alternatives. The work of Shriver,[4-6] which has also employed aluminum acids and carbonium ion precursors, has shown that bridging carbonyls are more basic then terminal carbonyls. More recently, the work of Fachinetti,[7] Keister,[8] and Shriver[9] employing low-valent metal clusters containing μ- and μ_3-CO ligands has shown that protonation (or alkylation) at carbonyl oxygen will sometimes induce an intramolecular electron transfer in which metal electrons serve to reduce CO to methanol or methane. Such transformations may mimic the Fischer–Tropsch activation of CO at a multimetallic site on a catalytic surface.

We report here our observations concerning both the fluxionality and basicity of $Cp_2Re_2(CO)_5$,[10] which contains the longest[11] metal–metal bond yet observed to be bridged by CO.[12]

Experimental Section

General Data. Reactions and spectroscopic studies were carried out under nitrogen with use of solvents dried by conventional methods. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded in the Fourier transform mode on a Varian XL 100-15 spectrometer. Some ^1H NMR spectra were also recorded on a Varian HR-220 spectrometer. $C_5H_5Re(CO)_3$ was prepared by two methods,[13,14] with the latter giving higher yield and purer product. $^{13}C\{^1H\}$ NMR (in $CDCl_3$ at 35 °C): δ 193.4 (CO), 84.3 (C_5H_5). ^1H NMR: δ 5.35 (in $CDCl_3$), 4.40 (in C_6D_6). $ReCl(CO)_5$ required in the latter synthesis was produced as reported.[15]

$(C_5H_4CH_3)Re(CO)_3$. This was prepared by the reaction of $NaC_5H_4CH_3\cdot MeOCH_2CH_2OMe$[16] (3.3 g, 17 mmol) with equimolar $ReCl(CO)_5$ in benzene. Following overnight reflux, the solvent was removed under vacuum. Sublimation (70 °C, 0.1 mmHg) of the solid residue yielded colorless crystals of the product in 80% yield. IR (in hexane): 2030 (s), 1935 (vs) cm^{-1}. ^1H NMR (in C_6D_6): δ 4.33 (s, ring protons), 1.57 (s, CH_3). Mass spectrum (EI): $(C_5H_4CH_3)Re(CO)_n^+$, n = 0–3. $^{13}C\{^1H\}$ NMR (in $CDCl_3$): δ 194.2 (CO), 106.5 (ipso C), 83.7 and 83.0 (unsubstituted ring carbons).

$(C_5H_5)_2Re_2(CO_5$ (Ia) was synthesized according to the literature.[10] Irradiation (254 nm, Rayonet reactor) in a quartz reactor tends to deposit the hexane-insoluble product on the outer reactor walls; this problem is minimized by employing a water-cooled glass spiral insert in the reactor, which has the effect of encouraging crystallization of the product on the cooled spiral. The IR and ^1H NMR (δ 4.67 in C_6D_6) agree with those reported.[10] The EI mass spectrum shows the ions $Cp_2Re_2(CO)_n^+$, n = 0–5. $^{13}C\{^1H\}$ NMR (CD_2Cl_2 with 0.05 M $Cr(acac)_3$): δ 207.48 (5 CO), 88.6 (C_5H_5) (at +25 and −83 °C). This compound and **Ib** are only mildly air sensitive in solution.

$(C_5H_4CH_3)_2Re_2(CO)_5$ (Ib) was synthesized analogously, by photolysis of $(C_5H_4Me)Re(CO)_3$ in hexanes. The solution IR (carbonyl region) is identical with that of Ia. ^1H NMR (220 MHz in CD_2Cl_2 at 16 °C): δ 5.22 and 5.14 (AA′BB′ pattern of two "triplets" (2 Hz splitting) due to ring protons), 2.08 (s, CH_3). $^{13}C\{^1H\}$ NMR (at −70 °C in CD_2Cl_2): δ 209.3 (5 CO), 108.3 (2, substituted ring carbons), 88.0 and 85.9 (4 each, ring carbons), 12.7 (2, CH_3).

Test of Dimer Scission. $(C_5H_4CH_3)Re(CO)_3$ (0.015 g, 0.044 mmol) and $(C_5H_5)_2Re_2(CO)_5$ (0.024 g, 0.037 mmol) were combined in 1 mL C_6D_6. After 50 h, the ^1H NMR was invariant (integration vs. an internal standard); no new peaks were observed.

Attempted Exchange of ^{13}CO with $Cp_2Re_2(CO)_5$. A THF solution of $Cp_2Re_2(CO)_5$ is stable (i.e., no $CpRe(CO)_3$ is produced) under 1

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