Organometallics 1992, *11*, 2521-2528

Table VII. Final Positional Parameters and Equivalent Thermal Parameters (Å²) for $[Rh\{(C_8H_{14})B(pz)_2\}(COD)]$ (6) (Esd's in Parentheses)[a]

atom	*x*	*y*	*z*	B_{eq}
Rh	0.54732 (4)	0.250	0.13165 (3)	3.876 (8)
N1	0.6380 (2)	0.1446 (2)	0.0489 (2)	3.74 (6)
N2	0.6701 (2)	0.1603 (2)	−0.0579 (2)	3.19 (6)
C1	0.6927 (4)	0.0681 (3)	0.0866 (4)	4.85 (9)
C2	0.7589 (3)	0.0349 (3)	0.0054 (3)	5.5 (1)
C3	0.7430 (3)	0.0949 (3)	−0.0840 (4)	4.43 (8)
C4	0.6595 (4)	0.250	−0.2552 (4)	3.8 (1)
C5	0.6180 (3)	0.1575 (3)	−0.3142 (3)	4.95 (9)
C6	0.5028 (4)	0.1376 (3)	−0.2997 (3)	4.83 (9)
C7	0.4623 (3)	0.1549 (3)	−0.1814 (3)	4.14 (8)
C8	0.5018 (4)	0.250	−0.1266 (4)	3.23 (9)
C9	0.4979 (4)	0.3521 (4)	0.2538 (4)	6.8 (1)
C10	0.4286 (4)	0.3516 (4)	0.1671 (4)	6.2 (1)
C11	0.3252 (5)	0.3031 (4)	0.1682 (6)	9.5 (2)
C12	0.4788 (6)	0.3031 (5)	0.3652 (4)	11.1 (2)
B	0.6235 (4)	0.250	−0.1255 (5)	2.9 (1)
H8	0.477 (3)	0.250	−0.056 (4)	1.1 (9)*
H9	0.557 (3)	0.096 (3)	0.252 (4)	4 (1)*
H10	0.433 (3)	0.401 (3)	0.115 (3)	4 (1)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(^1/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3)]$.

as reported in Table VII. Intensities were considered as observed if $F_o^2 \geq 3.0\sigma(F^2)$ and used for the resolution and refinement of the structure. A value of $F_o = 0.0$ was given to those reflections having negative net intensities. The structure was solved by the combination of Patterson and Fourier methods and refined by full-matrix least-squares procedures (the function minimized was $[\sum w(|F_o| - 1/k|F_c|)^2]$ with $w = [\sigma^2(F_o)]^{-1}$). No extinction correction was deemed to be necessary.

The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[23] In the final Fourier difference maps, most of the hydrogens could be located, in particular those bound to C8, C9, and C10. These hydrogen atoms, were considered to be chemically significant and therefore were refined, starting from the experimental coordinates using isotropic temperature displacements. The contribution of the remaining hydrogens, in their idealized positions (C–H = 0.95 Å, $B = 5.0$ Å²), was taken into account but not refined. Anisotropic temperature factors were used for all non-hydrogen atoms. Upon convergence (no parameter shift of $>0.2\sigma(p)$), the last Fourier difference map showed no significant feature. All calculations were carried out by using the SDP crystallographic package.[22] Final atomic coordinates and equivalent thermal factors are given in Table VII.

Acknowledgment. U.E.B. gratefully acknowledges the support of the "Forschungskommission der ETH Zürich" and A.A. acknowledges financial support from MURST. We thank Prof. P. S. Pregosin for valuable discussion.

Supplementary Material Available: Anisotropic displacement parameters (Table S1), calculated hydrogen positions (Table S2), and an extended list of bond distances and angles (Table S3) for 6 (10 pages). Ordering information is given on any current masthead page.

OM910688B

---

(23) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Reactions of the 17-Electron Complex $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ with Alkyl Halides

Celeste A. MacConnachie, James M. Nelson, and Michael C. Baird*

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

Received March 20, 1992

Solutions of the compound $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ react with a series of organic halides RX (R = Me, $CH_2CH{=}CH_2$, $CH_2CH{=}CHCO_2Me$, CH_2Ph, CH_2CO_2R' (R′ = Me, Et), CH_2CN, $CH(CO_2Me)_2$; X = Br, I) to form the corresponding alkyl- and halochromium compounds $\eta^5\text{-}C_5H_5Cr(CO)_3R$ and $\eta^5\text{-}C_5H_5Cr(CO)_3X$. The new alkylchromium compounds are characterized by elemental analyses where possible, otherwise by spectroscopic techniques and comparisons with the compounds synthesized by reactions of the same alkyl halides with $Na[\eta^5\text{-}C_5H_5Cr(CO)_3]$. In contrast, organic halides containing one or more β-hydrogen atoms, RCH_2CH_2X, react to form $\eta^5\text{-}C_5H_5Cr(CO)_3H$, $\eta^5\text{-}C_5H_5Cr(CO)_3X$, $RCH{=}CH_2$, and RCH_2Me. Since $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ is known to dissociate spontaneously in solution at ambient temperature to the highly reactive, 17-electron, metal-centered radical species $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$, it is suggested that the reactions involve initial halogen abstraction from the alkyl halides by $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$, followed, for alkyl halides containing no β-hydrogen atoms, by coupling of the resulting alkyl radical with a second molecule of $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$. For alkyl halides containing β-hydrogen atoms, analyses of product distributions are consistent with initial halogen abstraction by $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ from RCH_2CH_2X followed by H-atom abstraction from $RCH_2CH_2^\bullet$ to give $\eta^5\text{-}C_5H_5Cr(CO)_3H$ and olefin. As the concentration of $\eta^5\text{-}C_5H_5Cr(CO)_3H$ increases, a secondary process, in which the radical $RCH_2CH_2^\bullet$ abstracts an H-atom from $\eta^5\text{-}C_5H_5Cr(CO)_3H$, becomes competitive. Observed coalescence of the $\eta^5\text{-}C_5H_5$ ^1H NMR resonance of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ with those of $\eta^5\text{-}C_5H_5Cr(CO)_3X$ (X = H, Br, I) is interpreted in terms of facile X-atom exchange which also proceeds via X-atom abstraction processes by $[\eta^5\text{-}C_5H_5Cr(CO)_3\}$.

Although organotransition metal chemistry has long been dominated by compounds containing closed-shell, 18-electron configurations,[1] recent years have seen the development of a very extensive chemistry of electronically unsaturated, 17-electron complexes.[2] While most known examples of the latter class of paramagnetic, metal-centered radicals are unstable with respect to a wide variety of coupling, atom abstraction and disproportionation re-

---

(1) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(2) (a) Baird, M. C. *Chem. Rev.* 1988, *88*, 1217. (b) Trogler, W. C., Ed. *Organometallic Radical Process*; Elsevier: Amsterdam, 1990.

0276-7333/92/2311-2521$03.00/0

actions and, indeed, are known to participate as reactive intermediates in many types of reactions, several examples have proven sufficiently persistent that they have been isolated and characterized both spectroscopically and crystallographically.[2]

Of particular interest and importance in the exploration of the structures, bonding, and chemistry of 17-electron, organometallic compounds has been the series of persistent, chromium-centered radicals $\{\eta^5\text{-}C_5R_5Cr(CO)_2L\}$ (R = H, Me; L = CO, tertiary phosphine);[3] when L = CO, the radicals exist in solution in equilibrium with the corresponding diamagnetic, closed-shell dimers $[\eta^5\text{-}C_5R_5Cr(CO)_3]_2$ (eq 1).[3a,e,j,l] Since the monomer–dimer exchange

$$[\eta^5\text{-}C_5R_5Cr(CO)_3]_2 \rightleftarrows 2\{\eta^5\text{-}C_5R_5Cr(CO)_3\} \tag{1}$$

processes are rapid on the NMR time scale at ambient temperatures, much of the chemistry of both systems (R = H and Me) has been shown to reflect the reactivities of the much more labile monomers,[3a] a fact which we have exploited in investigations of substitution reactions of the dimers with a variety of tertiary phosphines.[3a,d–f,k]

As has been well established elsewhere, a very important class of reactions of main-group-element-centered radicals are those in which the radicals take part in a variety of atom abstraction processes.[4a–d] Analogous reactions have been also been observed with several transition-metal-centered radicals $\{ML_n^\bullet\}$ which, besides taking part in coupling reactions (eq 2, analogous to the reverse of eq 1), also take part in atom abstraction reaction reactions with alkyl halides (eq 3).[4e] In most cases, however, the fate of

$$2\{ML_n^\bullet\} \rightarrow [ML_n]_2 \tag{2}$$

$$\{ML_n^\bullet\} + RX \rightarrow XML_n + R^\bullet \tag{3}$$

$R^\bullet$ appears to be unknown, and it was thus with interest that we observed, during the course of our initial investigation of the chromium system,[3a] a reaction in which the radical $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ appeared to take part in a *stoichiometric* reaction analogous to eq 3, i.e.

$$[\eta^5\text{-}C_5H_5Cr(CO)_3]_2 + MeI \rightarrow \eta^5\text{-}C_5H_5Cr(CO)_3I + \eta^5\text{-}C_5H_5Cr(CO)_3Me \tag{4}$$

The two products were formed simultaneously and essentially quantitatively in tetrahydrofuran, and the mechanism suggested involved initial iodine abstraction by one molecule of $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ followed by coupling of the resulting methyl radical with a second molecule of $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$, i.e.

$$\{\eta^5\text{-}C_5H_5Cr(CO)_3\} + MeI \rightarrow \eta^5\text{-}C_5H_5Cr(CO)_3I + Me^\bullet \tag{5}$$

$$\{\eta^5\text{-}C_5H_5Cr(CO)_3\} + Me^\bullet \rightarrow \eta^5\text{-}C_5H_5Cr(CO)_3Me \tag{6}$$

The chromium system thus appeared to be the first for which the atom abstraction reactions of organo-transition-metal-centered radicals with organic halides could be readily studied in detail, and we now describe the results of a much more extensive investigation of the reactions of the dimer, $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, with a variety of organic halides. Although definitive conclusions regarding the mechanisms of the reactions must await a kinetic investigation which is currently in progress,[5] reasonable mechanisms are proposed on the basis of literature precedents, product distributions, and qualitative estimates of relative rates. We also describe apparently analogous reactions in which the radical $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ takes part in halogen and hydrogen atom exchange reactions with the compounds $\eta^5\text{-}C_5H_5Cr(CO)_3X$ (X = H, Br, I). Aspects of this work have been communicated previously.[3a,h]

Experimental Section

Syntheses were carried out under nitrogen by utilizing normal Schlenk techniques and dried, deaerated solvents. GC experiments were performed with a Hewlett Packard 5880A gas chromatograph equipped with a flame ionization detector. IR and ^1H NMR spectra were run on Bruker IFS-85 FT-IR and AM-400 FT-NMR spectrometers, respectively; unless otherwise specified, all discussions of NMR spectra below refer to ^1H spectroscopy. The compound $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ was prepared as in the literature.[3e]

All IR-monitored reactions were carried out at ambient temperature under nitrogen using benzene or toluene solutions $\approx$ 0.002–0.02 M in $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ and alkyl halide concentrations 2–3 times the total concentration of $\eta^5\text{-}C_5H_5Cr(CO)_3$. In a typical experiment, a solution of 20–200 mg of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ in 10–30 mL of benzene or toluene was mixed with 10–15 mL of solution containing the alkyl halide; IR spectra were obtained prior to mixing and at various time intervals as appropriate.

All NMR-monitored reactions were carried out at ambient temperature (unless otherwise specified) under nitrogen using benzene-d_6 or toluene-d_8 solutions, concentrations of $[\eta^5\text{-}C_5H_5Cr(CO)_3]$ in the range 0.02–0.2 M, and ratios of total chromium to alkyl halide $\approx$1:1. Typically a sample of 15–25 mg of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ was dissolved in 1–2 mL of deuterated solvent containing the alkyl halide. The solution was then transferred to an NMR tube sealed with a septum and placed in the probe of the NMR spectrometer. The procedure was normally carried out as quickly as possible, and acquisition of spectra normally began within 5 min of initial mixing of the reagents, continuing for suitable time intervals as appropriate. Residual solvent resonances were used as internal references for purposes of integrations, relaxation delays of 1.5 s being found to result in accurate integrations of the spectra. In all cases where organic products were identified by NMR spectroscopy, comparisons were made with spectra of authentic samples; in most cases, confirmation was achieved with GC analyses.

Reactions of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ with Alkyl Halides Containing No β-Hydrogen Atoms. Methyl Iodide. Within 4 h of addition of MeI to a toluene solution of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, the formation of $\eta^5\text{-}C_5H_5Cr(CO)_3I$ (ν(CO) at 2030, 1974, 1951 cm^{-1})[7a]

---

(3) (a) Cooley, N. A.; Watson, K. A.; Fortier, S.; Baird, M. C. *Organometallics* 1986, *5*, 2563. (b) Morton, J. R.; Preston, K. F.; Cooley, N. A.; Baird, M. C.; Krusic, P. J.; McLain, S. J. *J. Chem. Soc., Faraday Trans. 1* 1987, *83*, 3535. (c) Cooley, N. A.; Baird, M. C.; Morton, J. R.; Preston, K. F.; LePage, Y. *J. Magn. Reson.* 1988, *76*, 325. (d) Cooley, N. A.; MacConnachie, P. F. T.; Baird, M. C. *Polyhedron* 1988, *7*, 1965. (e) Jaeger, T. J.; Baird, M. C. *Organometallics* 1988, *7*, 2074. (f) Watkins, W. C.; Macartney, D. H.; Baird, M. C. *J. Organomet. Chem.* 1989, *377*, C52. (g) Jaeger, T. J.; Watkins, W. C.; MacNeil, J. H.; Fortier, S.; Watson, K. A.; Hensel, K.; Baird, M. C.; Preston, K. F.; Morton, J. R.; LePage, Y.; Charland, J.-P. *J. Am. Chem. Soc.* 1991, *113*, 542. (h) Goulin, C. A.; Huber, T. A.; Nelson, J. M.; Macartney, D. H.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* 1991, 798. (i) O'Callaghan, K.; Brown, S. J.; Page, J. A.; Baird, M. C.; Richards, T. C.; Geiger, W. E. *Organometallics* 1991, *10*, 3114. (j) Watkins, W. C.; Jaeger, T. J.; Kidd, C. E.; Fortier, S.; Baird, M. C.; Kiss, G.; Roper, G. C.; Hoff, C. D. *J. Am. Chem. Soc.* 1992, *114*, 907. (k) Watkins, W. C.; Macartney, D. H.; Baird, M. C.; McLain, S. J. *Organometallics*, in press. (l) McLain, S. J. *J. Am. Chem. Soc.* 1988, *110*, 643. (m) Krusic, P. J.; McLain, S. J.; Morton, J. R.; Preston, K. F. *J. Magn. Reson.* 1987, *74*, 72. (n) Madach, T.; Vahrenkamp, H. *Z. Naturforsch.* 1978, *33B*, 1301. (o) Madach, T.; Vahrenkamp, H. *Z. Naturforsch.* 1979, *34B*, 573. (p) Goh, L. Y.; D'Aniello, M. J.; Slater, S.; Muetterties, E. L.; Tavanaiepour, I.; Chang, M. I.; Fredrich, M. F.; Day, V. W. *Inorg. Chem.* 1979, *18*, 192. (q) Goh, L. Y.; Hambley, T. W.; Darensbourg, D. J.; Reibenspies, J. *J. Organomet. Chem.* 1990, *381*, 349. (r) Goh, L. Y.; Khoo, S. K.; Lim, Y. Y. *J. Organomet. Chem.* 1990, *399*, 115. (s) Kiss, G.; Zhang, K.; Mukerjee, S. L.; Hoff, C. D. *J. Am. Chem. Soc.* 1990, *112*, 5657. (t) Goh, L. Y.; Lim, Y. Y. *J. Organomet. Chem.* 1991, *402*, 209. (u) Adams, R. D.; Collins, D. E.; Cotton, F. A. *J. Am. Chem. Soc.* 1974, *96*, 749.

(4) (a) Kochi, J. K., Ed. *Free Radicals*; Wiley and Sons: New York, 1973; Vols. 1 and 2. (b) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978. (c) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, U.K., 1986. (d) Alfassi, Z. B., Ed. *Chemical Kinetics of Small Organic Radicals*; CRC Press: Boca Raton, FL, 1988; Vols. 1–4. (e) Brown, T. L. In *Organometallic Radical Process*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; p 67 (see also references therein).

(5) Huber, T. A.; Macartney, D. H.; Baird, M. C. Research in progress.

(6) Toluene-d_8 is much less expensive than tetrahydrofuran-d_8.

was quite evident from the appearance of weak absorptions at 2030 and 1974 cm^{-1}; a shoulder at 2006 cm^{-1} was also taken as evidence for the formation of η^5-$C_5H_5Cr(CO)_3Me$ (ν(CO) at 2006 (s), 1926 (s, br) cm^{-1}).[7b] The amounts of the products increased with time, the absorptions of η^5-$C_5H_5Cr(CO)_3Me$ being the strongest in the spectrum of the solution after 24 h. Other species included η^5-$C_5H_5Cr(CO)_3I$, residual $[\eta^5$-$C_5H_5Cr(CO)_3]_2$, and a significant amount of $[\eta^5$-$C_5H_5Cr(CO)_2]_2$ (ν(CO) at 1902 and 1878 cm^{-1}), formed by slow thermal decomposition of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$.[7c] The IR and NMR spectroscopic properties of η^5-$C_5H_5Cr(CO)_3Me$ were identical to those of an authentic sample prepared by reacting the salt, $Na[\eta^5$-$C_5H_5Cr(CO)_3]$, with MeI.[7b]

The reaction was also monitored by NMR spectroscopy, the formation of η^5-$C_5H_5Cr(CO)_3Me$ being apparent from the appearance of η^5-C_5H_5 and methyl resonances at δ 3.97 and 0.59,[7b] the formation of $[\eta^5$-$C_5H_5Cr(CO)_2]_2$ from a resonance at δ 4.22. It was found that ≈25% and ≈50% of the $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ had disappeared after 27 and 72 h, respectively. The compound $[\eta^5$-$C_5H_5Cr(CO)_2]_2$ formed somewhat faster than did η^5-$C_5H_5Cr(CO)_3Me$, but decomposition apparently also occurred and the yield of η^5-$C_5H_5Cr(CO)_3Me$ was only ≈10% after 72 h.

Allyl Bromide and Iodide. On addition of allyl iodide (3× excess) to a solution of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ in toluene, the color of the solution immediately changed from the deep green of the dimer to the deep purple of η^5-$C_5H_5Cr(CO)_3I$. Indeed, an IR spectrum obtained at this point exhibited the ν(CO) of the iodo compound at 2030 (s), 1974 (vs), and 1952 (m) cm^{-1}, as well as two other much weaker absorptions at 2004 and 1931 cm^{-1}; within 45 min, the absorptions at 2004 and 1931 cm^{-1} had disappeared. Reaction of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ with a slight deficiency of allyl iodide in toluene was also essentially finished on mixing of the reactants, but in this case the absorptions of η^5-$C_5H_5Cr(CO)_3I$ were accompanied by equally intense absorptions at 2004 (s) and 1931 (s, br) cm^{-1}. These frequencies are very similar to those of η^5-$C_5H_5Cr(CO)_3Me$ and thus are reasonably attributed to the η^1-allyl analogue, η^5-$C_5H_5Cr(CO)_3(\eta^1$-$CH_2CH{=}CH_2)$. Indeed, treatment of the salt, $Na[\eta^5$-$C_5H_5Cr(CO)_3]$, with allyl bromide in THF resulted in the formation of a solute with ν(CO) at 2003 (s) and 1929 (s, br) cm^{-1}, confirming the formation of η^5-$C_5H_5Cr(CO)_3(\eta^1$-$CH_2CH{=}CH_2)$. After 1.75 h, the intensities of the absorptions at 2004 and 1931 cm^{-1} had decreased somewhat, but the former was still evident in a spectrum run after 16 h. The latter spectrum (green solution) also exhibited the absorptions of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$.

Similar results were obtained on reaction of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ with allyl bromide, although in this case the reaction took 3–4 h to proceed to completion. In contrast to the situation in the presence of allyl iodide (see above), however, η^5-$C_5H_5Cr(CO)_3(\eta^1$-$CH_2CH{=}CH_2)$ is stable for several hours even in the presence of a 10× excess of allyl bromide; the bromo product, η^5-$C_5H_5Cr(CO)_3Br$, is much less thermally stable under these reaction conditions, and its absorptions had disappeared within 5 h, leaving only the ν(CO) of η^5-$C_5H_5Cr(CO)_3(\eta^1$-$CH_2CH{=}CH_2)$ apparent in the IR spectrum. The solution had by this time turned bright blue, the color of the product of decomposition of η^5-$C_5H_5Cr(CO)_3Br$; however, the non-carbonyl-containing material was not investigated further.

An NMR spectrum of the allyl product was obtained by removing under reduced pressure all volatile materials from a reaction mixture which contained (IR analysis) η^5-$C_5H_5Cr(CO)_3(\eta^1$-$CH_2CH{=}CH_2)$ but no η^5-$C_5H_5Cr(CO)_3Br$. The solid residue was dissolved in 3 mL of toluene-d_8 and eluted through a short column of silica gel into an NMR tube. The spectrum of the yellow solution exhibited resonances at δ 6.11 (m, 1 H, $-CH{=}$), 5.01 (d, J 16 Hz, 1 H, $=CH_2$), 4.75 (d, J 9 Hz, 1 H, $=CH_2$), 3.96 (s, 5 H, η^5-C_5H_5), 2.33 (d, J 9 Hz, 2 H, $-CH_2-$). These parameters are very similar to those of η^5-$C_5H_5Fe(CO)_2(\eta^1$-$CH_2CH{=}CH_2)$,[7d] thus confirming the assignments. However, on standing, the solution turned green, the resonances of η^5-$C_5H_5Cr(CO)_3(\eta^1$-$CH_2CH{=}CH_2)$ disappeared, and a broad resonance, attributable to the $[\eta^5$-$C_5H_5Cr(CO)_3]_2$–$\{\eta^5$-$C_5H_5Cr(CO)_3\}$ equilibrium mixture, appeared at δ 6.00. The formation of 1,5-hexadiene was confirmed by GC and NMR spectroscopy.

Ethyl 4-Bromocrotonate. Reaction of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ with $BrCH_2CH{=}CHCO_2Et$ in benzene was complete within minutes (IR analysis), but a shoulder at 2008 cm^{-1}, attributable to the anticipated product η^5-$C_5H_5Cr(CO)_3CH_2CH{=}CHCO_2Et$, weakened and disappeared much faster than did even the ν(CO) of η^5-$C_5H_5Cr(CO)_3Br$. A reaction was therefore run at 273 K in ethyl ether, followed by passing of the concentrated reaction mixture through a silica column maintained at 273 K with a water-cooled jacket. Elution with benzene to remove a greenish-brown solution of η^5-$C_5H_5Cr(CO)_3Br$ followed by elution with ethyl ether resulted in a yellow solution exhibiting ν(CO) in its IR spectrum at 2008 (s) and 1932 (s, br) cm^{-1}, attributed to η^5-$C_5H_5Cr(CO)_3CH_2CH{=}CHCO_2Et$. A complementary NMR experiment in toluene-d_8 showed that while the reaction was very slow at 273 K, it proceeded at a reasonable rate above 285 K to give a plethora of new resonances. This result also suggested that the organometallic product decomposed almost as fast as it formed, and the reaction was not investigated further.

Benzyl Bromide and Iodide. Immediately upon addition of benzyl bromide to a solution of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ in toluene, the color of the solution turned dark brown and absorbances of η^5-$C_5H_5Cr(CO)_3Br$ appeared in the IR spectrum. After 90 min, the absorbances of both $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ and η^5-$C_5H_5Cr(CO)_3Br$ had grown very weak, the solution had turned olive-green, and the IR spectrum was dominated by bands at 2002 (s) and 1927 (s, br) cm^{-1}, clearly to be assigned to the benzyl compound η^5-$C_5H_5Cr(CO)_3CH_2Ph$. Consistent with the assignment, monitoring of the reaction in toluene-d_8 showed that new singlets at δ 3.97 and 2.11 (relative intensities 5:2) appeared immediately on combination of the reactants and could be assigned to the η^5-C_5H_5 and CH_2 resonances, respectively, of η^5-$C_5H_5Cr(CO)_3CH_2Ph$. Interestingly, a singlet at δ 2.93, attributable to bibenzyl, was also apparent, suggesting that η^5-$C_5H_5Cr(CO)_3CH_2Ph$ undergoes homolysis as does the η^1-allyl analogue (see above). However, treatment of the salt, $Na[\eta^5$-$C_5H_5Cr(CO)_3]$, with benzyl iodide in THF resulted in a solute exhibiting ν(CO) at 2001 (s) and 1926 (s, br) cm^{-1}, also confirming the IR assignments.

Reaction of benzyl iodide with $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ in benzene-d_6 proceeded more rapidly, resonances at δ 7.36 (m), 3.99 (s), and 2.11 (s) being attributed to the η^5-$C_5H_5Cr(CO)_3CH_2Ph$, a singlet at δ 2.96 to bibenzyl. Benzyl chloride gave no indication of reacting with the dimer after 15 h.

Iodoacetonitrile. ICH_2CN reacts immediately with $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ in benzene to give a purple solution exhibiting ν(CO) at 2025 (s), 1973 (s), and 1952 (vs) cm^{-1} in the IR spectrum; although these correspond well to the ν(CO) of η^5-$C_5H_5Cr(CO)_3I$, the relative intensities are anomalous and clearly the solution contained another species. The solvent was therefore removed under reduced pressure, the dark residue was dissolved in a small amount of ethyl ether, and the solution was chromatographed on a silica column. A dark purple solution containing η^5-$C_5H_5Cr(CO)_3I$ eluted first, followed by a yellow fraction. On removal of the ether from the latter followed by dissolution in benzene, the IR spectrum was found to exhibit ν(CO) at 2027 (s) and 1946 (s, br) cm^{-1}. These absorbances are at almost the same frequencies as two of the original absorptions mentioned above, consistent with their being obscured in the spectrum of the reaction mixture. An NMR spectrum of the yellow substance exhibits resonances at δ 4.00 (s, 5 H) and 0.92 (s, 2 H), consistent with its formulation as the anticipated η^5-$C_5H_5Cr(CO)_3CH_2CN$.

Unfortunately, the isolated, solid compound decomposes at room temperature and elemental analyses could not be obtained. In an effort synthesize it via an alternative route, a suspension of 21 mg of $Na[\eta^5$-$C_5H_5Cr(CO)_3]$ (0.09 mmol) in benzene-d_6 was treated with 10 μL of ICH_2CN (0.14 mmol). Within minutes, the

---

(7) (a) Manning, A. R.; Thornhill, D. J. *J. Chem. Soc. A* **1971**, 637. (b) Alt, H. G. *J. Organomet. Chem.* **1977**, *124*, 167. (c) Hackett, P.; O'Neill, P. S.; Manning, A. R. *J. Chem. Soc., Dalton Trans.* **1974**, 1625. (d) Cutler, A.; Ehnholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495. (e) Medina, R. M.; Masaguer, J. R. *J. Organomet. Chem.* **1986**, *299*, 341. The compound formulated in this paper as η^5-$C_5H_5Cr(CO)_3Et$ exhibits a ^1H NMR spectrum (δ 4.81–4.38, m, η^5-C_5H_5; δ 3.61, q, CH_2; δ 1.11, t, Me) which is incompatible with the formulation although the reported IR data (ν(CO) 2012, 1933 cm^{-1}) are reasonable. For purposes of comparison, we have attempted to repeat the same synthesis of η^5-$C_5H_5Cr(CO)_3Et$ by treating the salt, $Na[\eta^5$-$C_5H_5Cr(CO)_3]$, with ethyl iodide; we obtained an unstable yellow material exhibiting ν(CO) at 2004 (s) and 1920 (s, br) cm^{-1} (THF), but with a ^1H NMR spectrum incompatible with the formulation η^5-$C_5H_5Cr(CO)_3Et$. This material is being investigated further.

resonances of η^5-$C_5H_5Cr(CO)_3CH_2CN$ at δ 0.92 and 4.00 appeared.

Methyl and Ethyl Bromoacetates. Reaction of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ with $BrCH_2CO_2Me$ in toluene was essentially complete (IR analysis) within a few hours, by which time most of the η^5-$C_5H_5Cr(CO)_3Br$ had also disappeared and the IR spectrum was dominated by ν(CO) at 2019 and 1948 cm^{-1}. The solvent was then removed under reduced pressure, the residue was extracted with ethyl ether, and the solution was chromatographed on a silica column to give a greenish-yellow fraction. The solvent was removed, and the resulting oil was induced to crystallize from pentane at 195 K (2-propanol–dry ice bath) to give a bright yellow solid. Anal. Calcd for $C_{11}H_{10}CrO_5$: C, 48.19; H, 3.68. Found: C, 48.60; H, 3.95. The IR spectrum of the purified η^5-$C_5H_5Cr(CO)_3CH_2CO_2Me$ in benzene exhibited ν(CO) at 2019 (s) and 1948 (s, br) cm^{-1}; the NMR spectrum in benzene-d_6, resonances at δ 4.19 (s, 5 H, η^5-C_5H_5), 3.46 (s, 3 H, Me), and 1.75 (s, 2 H, CH_2). This compound was also synthesized by treating a suspension of 21 mg of $Na[\eta^5$-$C_5H_5Cr(CO)_3]$ (0.09 mmol) in benzene-d_6 with 10 μL of $BrCH_2CO_2Me$ (0.14 mmol). Within minutes, the resonances of η^5-$C_5H_5Cr(CO)_3CH_2CO_2Me$ at δ 1.75, 3.46, and 4.19 appeared.

Similar procedures were followed for the reaction of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ with $BrCH_2CO_2Et$ in toluene. Although the resulting yellow product was too unstable for satisfactory elemental analyses to be carried out, the same material was obtained with ICH_2CO_2Et and by treating $Na[\eta^5$-$C_5H_5Cr(CO)_3]$ in benzene-d_6 with $BrCH_2CO_2Et$. The spectroscopic properties are clearly consistent with its formulation as η^5-$C_5H_5Cr(CO)_3CH_2CO_2Et$. IR (benzene): ν(CO) at 2019 (s), 1949 (s, br) cm^{-1}. NMR (benzene-d_6): δ 4.19 (s, 5 H, η^5-C_5H_5), 4.03 (q, *J* 7 Hz, 2 H, OCH_2), 1.80 (s, 2 H, $CrCH_2$), 1.06 (t, *J* 7 Hz, 3 H, Me).

Dimethyl Bromomalonate. Reaction of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ and $BrCH(CO_2Me)_2$ in benzene seemed complete (IR analysis) within a few minutes, the IR spectrum of the greenish-brown solution exhibiting ν(CO) of the bromo compound and new absorptions at 2029 and $\approx$1960 (sh) cm^{-1}. While the latter absorptions are at reasonable frequencies for the anticipated alkyl–chromium product, they weakened considerably over 1 h, suggesting low thermal stability. A low-temperature NMR experiment was therefore carried out; the reactants were combined at 193 K in toluene-d_8, and the solution was allowed to warm to 273 K in the spectrometer probe. New resonances attributable to η^5-$C_5H_5Cr(CO)_3CH(CO_2Me)_2$ appeared at δ 4.32 (s, 5 H, η^5-C_5H_5), 3.40 (s, 6 H, Me), and 3.20 (s, 1 H, CH). The compound was also prepared at 273 K in ethyl ether. The solution was concentrated and cannulated onto a silica column fitted with a water-cooled jacket held at 273 K. Benzene was used to elute a greenish-brown fraction containing η^5-$C_5H_5Cr(CO)_3Br$; ethyl ether, to elute a yellow solution of η^5-$C_5H_5Cr(CO)_3CH(CO_2Me)_2$ exhibiting ν(CO) at 2029 (s) and 1962 (s, br) cm^{-1}. Removal of the solvent under reduced pressure and dissolution of the yellow oil in benzene-d_6 gave a yellow solution which exhibited resonances at δ 4.35 (s, 5 H, η^5-C_5H_5), 3.42 (s, 6 H, Me), and 3.28 (s, 1 H, CH), but which then darkened as the solute decomposed. In an effort to synthesize the compound via an alternative route, a suspension of 21 mg of $Na[\eta^5$-$C_5H_5Cr(CO)_3]$ (0.09 mmol) in benzene-d_6 was treated with 20 mg of $BrCHC(CO_2Me)_2$ (0.95 mmol). Within minutes, the ν(CO) of η^5-$C_5H_5Cr(CO)_3CH(CO_2Me)_2$ at 2029 and 1962 cm^{-1} appeared.

Reactions of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ with Alkyl Halides Containing β-Hydrogen Atoms. Ethyl Iodide. The reaction of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ with EtI was very slow in toluene. Although the ν(CO) resonances of η^5-$C_5H_5Cr(CO)_3I$ were observed after 90 min and continued to gain intensity, the dimer was still the major species in solution after 24 h. A solution in toluene-d_8 was monitored by NMR spectroscopy for 72 h, only singlet resonances attributed to the hydride, η^5-$C_5H_5Cr(CO)_3H$ (δ −5.65[3d]), ethylene, and ethane being observed.

2-Iodopropane. A solution of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ and Me_2CHI turned from emerald green to deep purple-brown within 2 h, although some dimer still remained after 24 h. Monitoring of a reaction mixture in toluene-d_8 by NMR spectroscopy showed that the reaction was about 30% complete within 17 h and that propylene, propane (55:45 ratio), and hydride had formed. A spectrum run after 4 h at 230 K showed, on the basis of relative intensities of the η^5-C_5H_5 resonances, that the ratio of $[\eta^5$-$C_5H_5Cr(CO)_3H]$:$[\eta^5$-$C_5H_5Cr(CO)_3I]$ was $\approx$1:5; no resonance at δ $\approx$4 attributable to a propylchromium compound was observed.

A solution of 0.4 g of $Na[\eta^5$-$C_5H_5Cr(CO)_3]$ (1.8 mmol) and 183 μL of Me_2CHI in THF was stirred at room temperature for 1 h and then refluxed for 1.5 h. There was no apparent reaction (IR analysis).

2-Iodo-2-methylpropane. The solution of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ and Me_3CI turned from emerald green to deep purple-brown almost immediately, and the reaction was essentially complete within 35 min (IR analysis); the compounds η^5-$C_5H_5Cr(CO)_3H$ and η^5-$C_5H_5Cr(CO)_3I$ were the major carbonyl-containing products in the solution. NMR experiments (benzene-d_6 and toluene-d_8) demonstrated that, while isobutene and isobutane were formed, the ratio of isobutene to isobutane decreased from $\approx$15:1 initially to 55:45 at the end of the reaction (confirmed by GC analysis). The ratio of η^5-$C_5H_5Cr(CO)_3H$ to η^5-$C_5H_5Cr(CO)_3I$ decreased proportionately. On carrying out the reaction in the presence of isoprene, the final ratio of isobutene to isobutane increased to $\approx$7:1. On carrying out the reaction at 285 K, no resonance at δ $\approx$4 attributable to a butylchromium compound was observed.

2-Iodobutane. The IR spectrum of the reaction mixture of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ with MeCHIEt showed that η^5-$C_5H_5Cr(CO)_3H$ and η^5-$C_5H_5Cr(CO)_3I$ were the major products formed, while an NMR experiment suggested that the reaction proceeded somewhat more slowly than the reaction of 2-iodopropane (see above). Also formed were *n*-butane (20%), 1-butene (36%), *cis*-2-butene (6%), and *trans*-2-butene (38%).

1-Iodobutane, 1-Iodo-2-methylpropane, 1-Iodo-2,2-dimethylpropane, and 6-Iodo-1-Hexene. The IR spectra of the reaction mixtures of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ with *n*-BuI, ICH_2CHMe_2, Me_3CH_2I, and $CH_2{=}CH(CH_2)_4I$ showed that only very small amounts of η^5-$C_5H_5Cr(CO)_3I$ had formed after 24 h, and the reactions were not monitored further.

1,*n*-Diiodoalkanes (*n* = 1–5). Reaction of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ with CH_2I_2 was complete within 4 h to form η^5-$C_5H_5Cr(CO)_3I$, the only product identified, while reaction of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ with ICH_2CH_2I was very rapid, producing η^5-$C_5H_5Cr(CO)_3I$ and ethylene. Reactions of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ with $I(CH_2)_nI$ (n = 3–5) were very slow, producing small amounts of η^5-$C_5H_5Cr(CO)_3I$ and η^5-$C_5H_5Cr(CO)_3H$. These reactions were not investigated further.

1-(Bromoethyl)benzene. Within 15 min of combining a solution of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ with PhCHBrMe, the IR spectrum of the dark brown reaction mixture exhibited the ν(CO) of η^5-$C_5H_5Cr(CO)_3H$ and η^5-$C_5H_5Cr(CO)_3Br$, which were the major species observed. An NMR spectrum confirmed the presence of these two species, as well as of styrene and ethylbenzene (3:1 ratio). When the reaction was carried out in the presence of excess η^5-$C_5H_5Cr(CO)_3H$, the ratio of styrene to ethylbenzene was 1:3.

Ethyl 2-Bromo-2-methylpropionate. The reaction of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ with $BrCMe_2CO_2Et$ in benzene was essentially complete within 30 min, the major products being η^5-$C_5H_5Cr(CO)_3H$ and η^5-$C_5H_5Cr(CO)_3Br$ (IR analysis). An NMR experiment confirmed the presence of these two species and also demonstrated that the organic products were $CH_2{=}CMeCO_2Et$ and Me_2CHCO_2Et (4:1 ratio at the end of the reaction).

Ethyl 4-Bromobutyrate. The reaction of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ with $Br(CH_2)_3CO_2Et$ yielded only very small amounts of η^5-$C_5H_5Cr(CO)_3H$ and η^5-$C_5H_5Cr(CO)_3Br$ after 24 h (IR and NMR analysis) and was not monitored further.

Methyl and Ethyl 2-Bromopropionates. Reactions of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ with $MeCHBrCO_2Me$ and $MeCHBrCO_2Et$ in benzene were essentially complete within 3–4 h (IR analysis), η^5-$C_5H_5Cr(CO)_3H$ and η^5-$C_5H_5Cr(CO)_3Br$ being the major products. Monitoring of both reactions by NMR spectroscopy confirmed this conclusion, as well, ultimately, as the presence of either $CH_2{=}CHCO_2Me$ and $EtCO_2Me$ (1.1:1 ratio) or $CH_2{=}CHCO_2Et$ and $EtCO_2Et$ (1.6:1 ratio; confirmed by GC). In an NMR experiment carried out at 285 K, resonances attributable to η^5-$C_5H_5Cr(CO)_3CHMeCO_2Me$ were observed at δ 4.20 (s, 5 H, η^5-C_5H_5), 3.57 (s, 3 H, OMe), 2.95 (q, *J* 8 Hz, 1 H, CH), and 1.55 (d, *J* 8 Hz, 3 H, Me). The resonances of $CH_2{=}CHCO_2Me$ and $EtCO_2Me$ appeared on raising the temperature to 290 K, but the resonances of η^5-$C_5H_5Cr(CO)_3CHMeCO_2Me$ broadened and decreased in intensity at 295 K.

Methyl and Ethyl 2-Bromobutyrates. Reactions of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ with both $EtCHBrCO_2Me$ and $EtCHBrCO_2Et$ in benzene required several hours to proceed to completion (IR analysis), $\eta^5\text{-}C_5H_5Cr(CO)_3H$ and $\eta^5\text{-}C_5H_5Cr(CO)_3Br$ being the major products. NMR monitoring of both reactions confirmed this conclusion, as well, ultimately, as the presence of either $MeCH{=}CHCO_2Me$ and $n\text{-}PrCO_2Me$ (1.1:1 ratio) or $MeCH{=}CHCO_2Et$ and $n\text{-}PrCO_2Et$ (3:1 ratio; confirmed by GC).

Unsuccessful Reactions of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$. No reactions of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ were observed after 10 h with the following potential substrates: 2-bromopentane, (2-bromoethyl)benzene, 2-methylallyl chloride, benzyl chloride, bromobenzene.

Results and Discussion

Although reactions of alkyl halides with $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ generally proceed much more rapidly in tetrahydrofuran than in benzene or toluene, the latter solvents were chosen for screening many of the reactions both because we wished to be able to monitor the processes at ambient and low temperatures utilizing NMR spectroscopy[6] and because the slow rates in the less polar solvents made it more readily possible to make qualitative rate comparisons (see below). In those cases where reactions on a synthetic scale were attempted, the more polar solvent ethyl ether was utilized. For most of the reactions monitored for long periods of time, we observed slow thermal decomposition of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ to form the dicarbonyl dimer, $[\eta^5\text{-}C_5H_5Cr(CO)_2]_2$ (in toluene: ν(CO) 1902, 1878 cm^{-1}; $\eta^5\text{-}C_5H_5$ chemical shift δ 4.25).[7c]

Exchange Processes of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ with $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ and $\eta^5\text{-}C_5H_5Cr(CO)_3X$ (X = H, Br, I). A complication in the use of NMR spectroscopy to monitor reactions of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ with organic halides is the monomer–dimer exchange process of eq 1, which is rapid on the NMR time scale at ambient temperature and which thus results in coalescence of the resonances and averaging of the chemical shifts of $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ (δ unknown but >30) and $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ (δ 4.02 at 228 K in toluene-d_6). This behavior has been described previously[3d,j,t] and results in observed $\eta^5\text{-}C_5H_5$ resonances whose chemical shifts and line widths are both temperature- and concentration-dependent over a range of concentrations and at all temperatures above that at which the $\eta^5\text{-}C_5H_5$ resonance of the dimer begins to undergo exchange broadening. Since the latter is accompanied by chemical shift changes,[3u] none of the usual NMR spectroscopic approaches for estimating rate constants[8] can be applied to the system, although the activation energy for the exchange process is clearly very low.

A further complication involves atom-exchange processes between the radical, $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$, and both the hydride, $\eta^5\text{-}C_5H_5Cr(CO)_3H$,[3a] and the halides, $\eta^5\text{-}C_5H_5Cr(CO)_3Br$ and $\eta^5\text{-}C_5H_5Cr(CO)_3I$ (eq 7). These exchange

$$\begin{gathered}\eta^5\text{-}C_5H_5Cr(CO)_3X + \{\eta^5\text{-}C_5H_5Cr'(CO)_3\} \rightleftharpoons \\ \{\eta^5\text{-}C_5H_5Cr(CO)_3\} + \{\eta^5\text{-}C_5H_5Cr'(CO)_3\}X \quad (7) \\ X = H, Br, I\end{gathered}$$

reactions may involve an initial donor interaction of electron density on X with the singly occupied orbital (SOMO) of $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$, similar to the type of 19-electron, intermediate/transition state postulated elsewhere as a key species in associative substitution reactions of many metal-centered radicals.[9] For the the exchange processes under consideration here, we envisaged symmetric transition states, as shown in eq 8. These exchange

$$\begin{gathered}\left\{\eta^5\text{-}C_5H_5Cr(CO)_3X{:}\rightarrow Cr'(CO)_3(\eta^5\text{-}C_5H_5)\right\} \\ \uparrow\downarrow \\ \left\{\eta^5\text{-}C_5H_5Cr(CO)_3\cdots X\cdots Cr'(CO)_3(\eta^5\text{-}C_5H_5)\right\} \\ \uparrow\downarrow \\ \{\eta^5\text{-}C_5H_5Cr(CO)_3\} + XCr'(CO)_3(\eta^5\text{-}C_5H_5) \quad (8)\end{gathered}$$

processes are also rapid on the NMR time scale at ambient temperature and, combined with the monomer–dimer exchange of eq 1, result in coalescence of the $\eta^5\text{-}C_5H_5$ resonance of the dimer with those of the hydride and the halides. Although we have briefly investigated the variable-temperature behavior (chemical shifts, line widths) of approximately equimolar solutions of hydride and dimer, here also rate constants cannot be satisfactorily estimated; however, the activation energies are clearly small. Our qualitative results are thus consistent with the reported activation parameters of similar atom-exchange processes of the molybdenum and tungsten analogues, $\{\eta^5\text{-}C_5H_5M(CO)_3\}$ (M = Mo, W), which have been measured and found to be very small.[10] We have also compared the effects of monomer/dimer concentrations on the line widths of the $\eta^5\text{-}C_5H_5$ resonances of the hydride and the deuteride, $\eta^5\text{-}C_5H_5Cr(CO)_3D$. The results suggest that the rate of hydrogen atom exchange is higher and thus a kinetic isotope effect appears to pertain, consistent with the mechanism proposed in eq 8.

As we have shown in the Experimental Section, all reactions of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ with alkyl halides yield the halo compounds, $\eta^5\text{-}C_5H_5Cr(CO)_3X$, while all reactions with alkyl halides containing one or more hydrogen atoms on C2 (β-hydrogen atoms) also invariably result in the formation of $\eta^5\text{-}C_5H_5Cr(CO)_3H$. The result in such cases, if a reaction is monitored by NMR spectroscopy at ambient temperature, is an observed $\eta^5\text{-}C_5H_5$ resonance whose chemical shift and line width are weighted averages of those of up to four different species (monomer, dimer, hydride, halide). In most cases described below, the initial resonance parameters reflect the equilibrium described by eq 1, the chemical shift and line width being respectively $\approx\delta$ 4.5–6.0 and 20–30 Hz.

As a reaction of an alkyl halide proceeds, the ratios of monomer to dimer and $\eta^5\text{-}C_5H_5Cr(CO)_3X$ to dimer (X = H, Br, I) both increase, the net result being that the averaged $\eta^5\text{-}C_5H_5$ resonance gradually moves to higher field as $\eta^5\text{-}C_5H_5Cr(CO)_3H$ and $\eta^5\text{-}C_5H_5Cr(CO)_3Br$ or $\eta^5\text{-}C_5H_5Cr(CO)_3I$ are formed. Decoalesced $\eta^5\text{-}C_5H_5$ resonances of the diamagnetic exchange partners $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ and $\eta^5\text{-}C_5H_5Cr(CO)_3X$ (X = H, Br, I) may be observed at about 230 K, and in several cases we have identified and estimated the relative concentrations of these compounds in this way during a reaction. Although the $\eta^5\text{-}C_5H_5$ resonances of the hydride and halide compounds are not normally sufficiently separated to be resolved, the relative amounts of hydride can always be determined by integrating the high-field hydride resonance of this compound. To our disappointment, $\eta^5\text{-}C_5H_5$ resonances of the alkyl compounds remained decoalesced in all experiments.

An interesting and very useful property of the bromo compound, $\eta^5\text{-}C_5H_5Cr(CO)_3Br$, was discovered when, for purposes of comparison, it was prepared by treating a toluene solution of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ with an equimolar amount of bromine. Although the reaction was instanta-

---

[8] (a) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982. (b) Stengle, T. R.; Langford, C. H. *Coord. Chem. Rev.* **1967**, *2*, 349.

[9] (a) Trogler, W. C. In *Organometallic Radical Process*; Trogler, W. C., Ed.; Elsevier: Amsterdam, 1990; p 306 (see also references therein). (b) Tyler, D. R. *Acc. Chem. Res.* **1991**, *24*, 325.

[10] Song, J.-S.; Bullock, R. M.; Creutz, C. *J. Am. Chem. Soc.* **1991**, *113*, 9862.

neous, the solution remained green and the IR spectrum exhibited ν(CO) of both the dimer and the product (2043, 1988, 1960 cm^{-1});[7a] thus it would seem that η^5-$C_5H_5Cr(CO)_3Br$ also reacts with bromine, forming a non-carbonyl-containing compound. An additional 2 equiv of bromine was then added to give a bright blue solution, the IR spectrum of which exhibited only the ν(CO) of η^5-$C_5H_5Cr(CO)_3Br$, although this compound is not reported to be blue.[7a] On standing for several hours, the solution became an even more vibrant blue and the ν(CO) in the IR spectrum disappeared, although the species in solution has not been investigated further.

In all reactions of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ with alkyl bromides, we have found, fortuitously, that the ν(CO) of η^5-$C_5H_5Cr(CO)_3Br$ disappeared within a short time of their appearance, thus facilitating identification of other compounds absorbing at similar frequencies. All such solutions also turned bright blue, although the nature of the blue species in solution was not ascertained. An NMs spectrum of a benzene-d_6 solution of the bright blue residue obtained by removal of the solvent from the $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$–bromine reaction exhibited no resonances. This result suggests that the final product is paramagnetic, but it was not investigated further.

We have also found that treatment of a toluene solution of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ with anhydrous HCl results in formation of the hydride, η^5-$C_5H_5Cr(CO)_3H$, identified by IR spectroscopy, and a very unstable species, presumably η^5-$C_5H_5Cr(CO)_3Cl$ (ν(CO) $\approx$2050, 1967 cm^{-1}). The iodo compound, η^5-$C_5H_5Cr(CO)_3I$, on the other hand, is much more thermally stable[7a] and remains in solution for over 1 day, at least.

Reactions of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ with Alkyl Halides. Reactions of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ with alkyl halides not containing β-hydrogen atoms appear in all cases to proceed essentially as in eq 9. The compound η^5-$C_5H_5Cr(CO)_3Me$

$$[\eta^5\text{-}C_5H_5Cr(CO)_3]_2 + RX \rightarrow \eta^5\text{-}C_5H_5Cr(CO)_3R + \eta^5\text{-}C_5H_5Cr(CO)_3X \quad (9)$$

$$R = Me,\ CH_2CH{=}CH_2,\ CH_2CH{=}CHCO_2Et,\ CH_2Ph,\ CH_2CO_2R'\ (R' = Me, Et),\ CH_2CN,\ CH(CO_2Me)_2$$

is known and was identified by comparison with an authentic sample,[7b] while the new compound η^5-$C_5H_5Cr(CO)_3CH_2CO_2Me$ was satisfactorily characterized by both elemental analyses and spectroscopic methods. The other new compounds were all found to be thermally unstable at ambient temperature so that satisfactory elemental analyses could not be obtained. However, several could also be synthesized via a reasonable alternative route, involving reactions of the salt, $Na[\eta^5\text{-}C_5H_5Cr(CO)_3]$, with the various organic halides. In all cases, the IR and/or NMR spectroscopic properties were fully compatible with the suggested formulations (see Experimental Section).

We present in Table I a list of ν(CO) and $\delta(\eta^5\text{-}C_5H_5)$ for purposes of comparison. As can be seen, there is a very reasonable correlation between the electronegativities of the ligands R and the carbonyl stretching frequencies of the compounds, consistent with the proposed familial relationships. The cyclopentadienyl chemical shifts are also reasonably consistent.

The mode(s) of decomposition was (were) not ascertained in all cases, but the η^1-allyl and benzyl compounds, respectively, formed 1,5-hexadiene and bibenzyl, the anticipated products of homolysis of the Cr–C bonds. Unfortunately, the NMR spectra of the decomposition products of the alkyl compounds containing cyano or ester groups were invariably very broad, making identification of the materials in solution very difficult. These reactions were not investigated further.

Table I. Selected Spectroscopic Properties of the Compounds η^5-$C_5H_5Cr(CO)_3R$

R	ν(CO) (cm^{-1})	$\delta(\eta^5\text{-}C_5H_5)$
Br	2043 (s), 1988 (s), 1960 (m)	
I	2030 (s), 1974 (s), 1951 (m)	3.98
$CH(CO_2Me)_2$	2029 (s), 1962 (s, br)	4.32
CH_2CN	2027 (s), 1946 (s, br)	4.00
CH_2CO_2Et	2019 (s), 1949 (s, br)	4.19
CH_2CO_2Me	2019 (s), 1948 (s, br)	4.19
H	2012 (s), 1925 (s, br)	3.95
Me	2006 (s), 1926 (s, br)	3.97
$CH_2CH{=}CHCO_2Me$	2008 (s), 1932 (s, br)	4.20
$CH_2CH{=}CH_2$	2004 (s), 1931 (s, br)	3.96
CH_2Ph	2002 (s), 1927 (s, br)	3.97

As suggested in the Introduction, the chemistry of eq 9 may involve the sequence of reactions described by eqs 1, 10, and 11. Thus dissociation of the dimer, $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, results in the formation of two monomers,

$$[\eta^5\text{-}C_5H_5Cr(CO)_3]_2 \rightleftharpoons 2\{\eta^5\text{-}C_5H_5Cr(CO)_3\} \quad (1)$$

$$\{\eta^5\text{-}C_5H_5Cr(CO)_3\} + RX \rightarrow \eta^5\text{-}C_5H_5Cr(CO)_3X + R^\bullet \quad (10)$$

$$\{\eta^5\text{-}C_5H_5Cr(CO)_3\} + R^\bullet \rightarrow \eta^5\text{-}C_5H_5Cr(CO)_3R \quad (11)$$

$\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$. Reaction of the monomer and RX, possibly involving donation of a lone pair on X to the SOMO of the monomer, as suggested above for the atom-exchange reactions of the monomer with η^5-$C_5H_5Cr(CO)_3H$, η^5-$C_5H_5Cr(CO)_3Br$, and η^5-$C_5H_5Cr(CO)_3I$, then results in formation of η^5-$C_5H_5Cr(CO)_3X$ and the alkyl radical, $R^\bullet$. The latter then has in principle several possibilities for further reaction[4] but is very effectively scavenged by a second molecule of $\{\eta^5\text{-}C_5H_5Cr(CO)_3\}$ since the compounds η^5-$C_5H_5Cr(CO)_3R$ appear to be formed in yields comparable to those of η^5-$C_5H_5Cr(CO)_3X$.

Reactions of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ with alkyl halides containing one or more β-hydrogen atoms appear in most cases to proceed essentially as in eq 12.

$$[\eta^5\text{-}C_5H_5Cr(CO)_3]_2 + RCH_2CH_2X \rightarrow \eta^5\text{-}C_5H_5Cr(CO)_3H + \eta^5\text{-}C_5H_5Cr(CO)_3X + RCH_2Me + RCH{=}CH_2 \quad (12)$$

For reasons which are not at present clear, alkyl halides reacting as in eq 12 do not appear to readily participate in the type of radical coupling reaction of eq 11. Thus careful scrutiny of the NMR spectra of reaction mixtures of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ with Me_2CHI and Me_3CI at 285 K yielded no hint of η^5-C_5H_5 resonances at $\delta \approx 4$, which would be characteristic of the alkylchromium compounds. Only in the case of the reaction of $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ with $BrCHMe(CO_2Me)$ at 285 K was there observed the formation of an alkyl compound containing β-hydrogen atoms; η^5-$C_5H_5Cr(CO)_3CHMe(CO_2Me)$ is presumably stabilized electronically[11] by the strongly electron-withdrawing ester group. In almost all cases, the product distributions seem better rationalized on the basis of the chemistry of eqs 13–15. Thus abstraction of a halogen atom by $\{\eta^5$-

$$\{\eta^5\text{-}C_5H_5Cr(CO)_3\} + RCH_2CH_2X \rightarrow \eta^5\text{-}C_5H_5Cr(CO)_3X + RCH_2CH_2^\bullet \quad (13)$$

$$\{\eta^5\text{-}C_5H_5Cr(CO)_3\} + RCH_2CH_2^\bullet \rightarrow \eta^5\text{-}C_5H_5Cr(CO)_3H + RCH{=}CH_2 \quad (14)$$

$$\eta^5\text{-}C_5H_5Cr(CO)_3H + RCH_2CH_2^\bullet \rightarrow \{\eta^5\text{-}C_5H_5Cr(CO)_3\} + RCH_2Me \quad (15)$$

---

[11] Electron-withdrawing groups such as fluorine are well-known for their ability to stabilize metal alkyl compounds. See Elschenbroich, Ch.; Salzer, A. *Organometallics*; VCH: Weinheim, 1989; p 204.

$C_5H_5Cr(CO)_3\}$ would occur as before (eq 13), but subsequent radical coupling to give η^5-$C_5H_5Cr(CO)_3CH_2CH_2R$ does not appear to be competitive with hydrogen abstraction from $RCH_2CH_2^{\bullet}$ by $\{\eta^5$-$C_5H_5Cr(CO)_3\}$ to give hydride and olefin (eq 14). However, as the concentration of the hydride increases, a secondary process in which the organic radical formed in eq 13 abstracts the hydride hydrogen of η^5-$C_5H_5Cr(CO)_3H$ to give the saturated hydrocarbon, becomes competitive. These two reactions must be very fast to compete with other possible radical processes and, with thermodynamic data from the literature,[12] including the Cr–H bond dissociation energy (257 kJ mol^{-1}) of η^5-$C_5H_5Cr(CO)_3H$,[3e] it can be shown that the chemistry of eqs 14 and 15 (R = H) would be exothermic by about 104 and 163 kJ mol^{-1}, respectively.

Also supporting the proposed mechanism are observations that the ratios of olefins to saturated organic products and of η^5-$C_5H_5Cr(CO)_3I$ to η^5-$C_5H_5Cr(CO)_3H$ were in several cases found to be >1. In addition, the ratio of isobutylene to isobutane decreased drastically and the amount of η^5-$C_5H_5Cr(CO)_3H$ decreased proportionately as the reaction of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ with 2-iodo-2-methylpropane proceeded. Complementing this result, addition of the hydride scavenger, isoprene,[3d] resulted in almost complete conversion of the hydrocarbon moiety to isobutylene while addition of excess η^5-$C_5H_5Cr(CO)_3H$ to the reaction of dimer with (1-bromoethyl)benzene resulted in a significant decrease in the proportion of olefin product. Furthermore, as reported previously,[3h] reaction of $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ with $(CD_3)_2CHI$ gives η^5-$C_5H_5Cr(CO)_3D$ and both propene and propane labeled appropriately.

It seems unlikely that the products are formed via coupling of the organic and chromium-centered radicals, followed by either homolysis of the chromium–carbon bond or β-elimination to give olefin and η^5-$C_5H_5Cr(CO)_3H$. As shown above, attempts to detect the formation of η^5-$C_5H_5Cr(CO)_3R$ (R = $CHMe_2$, CMe_3) at 285 K were unsuccessful, and η^5-$C_5H_5Cr(CO)_3CHMe(CO_2Me)$, presumably stabilized electronically, is the only alkylchromium compound containing β-hydrogen atoms for which we have evidence; it, however, is unstable and decomposes at 290 K.

In light of the fact that η^5-$C_5H_5Cr(CO)_3CH_2Ph$ and η^5-$C_5H_5Cr(CO)_3CH_2CH{=}CH_2$ are sufficiently robust that they can be isolated for at least a brief time at ambient temperature before undergoing apparent homolysis, it seems most improbable that the other simple alkyl analogues are less stable and would undergo spontaneous homolysis at even lower temperatures. Thus the Mo–X bond dissociation energies of the series of analogous molybdenum compounds η^5-$C_5H_5Mo(CO)_3X$ have been found experimentally to be 276 kJ mol^{-1} (X = H), 196 kJ mol^{-1} (Me), 155 kJ mol^{-1} (Et), and 134 kJ mol^{-1} ($PhCH_2$),[13] suggesting that the Cr–Et bond could be as much as 20 kJ mol^{-1} stronger than the Cr–CH_2Ph bond.

The only relevant Cr–X bond dissociation energy which has been reported is that of η^5-$C_5H_5Cr(CO)_3H$, for which a value of 257 kJ mol^{-1}, only 19 kJ mol^{-1} less than for its molybdenum analogue, has been found.[3e] If this decrease is typical of differences between chromium and molybdenum, then the anticipated Cr–CH_2Ph bond strength is far too large for homolysis to be facile unless entropy changes are a significant factor. We have shown that entropy factors related to a release of strain in the dimeric molecules $[\eta^5$-$C_5R_5Cr(CO)_3]_2$ (R = H, Me) and arising from the comcomitant increase in rotational freedom in the corresponding monomers provide a major impetus for dissociation of the dimers.[3j] Thus it seems quite possible that similar entropy factors will also contribute to homolytic destabilization of alkylchromium compounds relative to similar compounds of the larger molybdenum. A kinetics investigation of the decomposition of the compounds η^5-$C_5H_5Cr(CO)_3R$ (R = $PhCH_2$, $CH_2CH{=}CH_2$) is currently underway.[5]

A β-elimination process seems even more unlikely a route for decomposition of alkylchromium compounds containing β-hydrogen atoms, since monoolefins of the type which would be formed do not undergo hydrogen-transfer reactions with η^5-$C_5H_5Cr(CO)_3H$ and thus the saturated organic products observed would not be formed via this route. Intermolecular β-hydrogen abstraction seems unlikely for the same reason, and indeed, we find that $\{\eta^5$-$C_5H_5Cr(CO)_3\}$ does not react with η^5-$C_5H_5Fe(CO)_2Et$. It also seems unlikely that the organic products could result from free radical disproportionation, since this type of reaction would also result in products of radical combination,[14] which are not observed.

On the other hand, although we have not yet accumulated accurate kinetic data for the reactions described here, most reactions were in fact monitored under reasonably constant conditions of solvent, temperature, and concentration. Qualitatively, at least, the relative rates of the reactions were found to vary in the following orders: RCl < RBr < RI; MeI < EtI < MeEtCHI $\approx$ Me_2CHI < Me_3CI $\approx$ $CH_2CH{=}CH_2I$ $\approx$ $PhCH_2I$; $PhCH_2Br$ < PhMeCHBr; ICH_2CN > $BrCH(CO_2Me)_2$ > $BrCH_2CH{=}HCO_2Et$ ~ $BrC(Me)_2CO_2Et$ > $RCH(Br)CO_2R$ (R = Me, Et) > ICH_2CO_2Et > $BrCH_2CO_2R$ (R = Me, Et). The compounds n-BuI, Me_2CHCH_2I, Me_3CCH_2I, $PhCH_2CH_2Br$, $CH_2{=}CMeCH_2Cl$, $PhCH_2Cl$, and PhBr reacted exceedingly slowly or not at all, and thus the reaction rates correlate inversely with the relative carbon–halogen bond strengths,[15] consistent with the proposed mechanisms. It was also found that the reactions of EtI, Me_2CHI, and MeEtCHI with $[\eta^5$-$C_5H_5Cr(CO)_3]_2$ were all much faster than the corresponding reactions with $Na[\eta^5$-$C_5H_5Cr(CO)_3]$, showing that the anion, formed perhaps via disproportionation,[3d] was not a factor in the observed reactions.

Indeed, rather similar trends have been observed for analogous reactions of alkyl halides RX with alkyl,[16a] phenyl,[16b] and tributyltin radicals,[16b] as well as with the metal-centered radicals $\{Re(CO)_4L\}$ (L = PMe_3, $P(O$-i-$Pr)_3$),[16c] $[Co(CN)_5]^{3-}$,[16d] Rh(tetraphenylporphinato),[16e] and $Rh(dimethylglyoximato)_2PPh_3$.[16f] The compound Rh(tetraphenylporphinato) forms rhodium(III) complexes of the type [Rh(tetraphenylporphinato)R]X but not Rh(tetraphenylporphinato)X;[16e] the cobalt complex $[Co(CN)_5]^{3-}$, $[Co(CN)_5R]^{3-}$, $[Co(CN)_5X]^{3-}$, $[Co(CN)_5H]^{3-}$, olefins, and alkanes, depending on the nature of R.[16d]

---

[12] (a) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986. (b) Colussi, A. J. In *Chemical Kinetics of Small Organic Radicals*; Alfassi, Z. B., Ed.; CRC Press: Boca Raton, FL, 1988; Vol. 1, p 25.

[13] Nolan, S. P.; Lopez De La Vega, R.; Mukerjee, S. L.; Gonzalez, A. A.; Zhang, K.; Hoff, C. D. *Polyhedron* **1988**, *7*, 1491.

[14] Alfassi, Z. B. In *Chemical Kinetics of Small Organic Radicals*; Alfassi, Z. B., Ed.; CRC Press: Boca Raton, FL, 1988; Vol. 1, p 129.

[15] (a) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465. (b) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970. (c) Benson, S. W. *Thermochemical Kinetics*; Wiley and Sons: New York, 1968.

[16] (a) Curran, D. P.; Bosch, E.; Kaplan, J.; Newcomb, M. *J. Org. Chem.* **1989**, *54*, 1826. (b) Castelhano, A. L.; Griller, D. *J. Am. Chem. Soc.* **1982**, *104*, 3655 and references therein. (c) Lee, K.-W.; Brown, T. L. *J. Am. Chem. Soc.* **1987**, *109*, 3269. (d) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1969**, *91*, 582. (e) Anderson, J. E.; Yao, C.-L.; Kadish, K. M. *J. Am. Chem. Soc.* **1987**, *109*, 1106. (f) Howes, K. R.; Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1988**, *27*, 3147.

Interestingly, details of the modes of reactions of the various types of metal-centered radicals with alkyl halides appear to differ somewhat from that proposed here for the $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$ system; a mechanistic investigation of the latter is underway.[5]

Acknowledgment. Financial assistance from the National Sciences and Engineering Research Council of Canada (operating and equipment grants to M.C.B.) and Alcan International (fellowship to C.A.M.) made this research possible. We also thank M. Koeslag and T. A. Huber for laboratory assistance.

Registry No. $\eta^5\text{-}C_6H_5Cr(CO)_3Br$, 32628-92-5; $\eta^5\text{-}C_5H_5Cr(CO)_3I$, 32628-88-9; $\eta^5\text{-}C_5H_5Cr(CO)_3CH(CO_2Me)_2$, 141685-75-8; $\eta^5\text{-}C_5H_5Cr(CO)_3CH_2CN$, 141685-76-9; $\eta^5\text{-}C_5H_5Cr(CO)_3CH_2CO_2Et$, 141685-77-0; $\eta^5\text{-}C_6H_5Cr(CO)_3CH_2CO_2Me$, 141685-78-1; $\eta^5\text{-}C_5H_5Cr(CO)_3H$, 36495-37-1; $\eta^5\text{-}C_5H_5Cr(CO)_3Me$, 41311-89-1; $\eta^5\text{-}C_5H_5Cr(CO)_3CH_2CH{=}CHCO_2Me$, 141685-79-2; $\eta^5\text{-}C_5H_5Cr(CO)_3CH_2CH{=}CH_2$, 135571-87-8; $\eta^5\text{-}C_5H_5Cr(CO)_3CH_2Ph$, 98316-23-5; $\eta^5\text{-}C_5H_5Cr(CO)_3CH_2CH{=}CHCO_2Et$, 141685-80-5; $\eta^5\text{-}C_5H_5Cr(CO)_3CHMeCO_2Me$, 141685-81-6; $[\eta^5\text{-}C_5H_5Cr(CO)_3]_2$, 12194-12-6; $BrCH(CO_2Me)_2$, 868-26-8; ICH_2CN, 624-75-9; $BrCH_2CO_2Et$, 105-36-2; $BrCH_2CO_2Me$, 96-32-2; $BrCH_2Ph$, 100-39-0; $BrCH_2CH{=}CHCO_2Me$, 1117-71-1; $BrCH_2CH{=}CH_2$, 106-95-6; $ICH_2CH{=}CH_2$, 556-56-9; ICH_2Ph, 620-05-3; EtI, 75-03-6; Me_2CHI, 75-30-9; Me_3CI, 558-17-8; MeEtCHI, 513-48-4; *n*-BuI, 542-69-8; CH_2I_2, 75-11-6; ICH_2CH_2I, 624-73-7; $ICH_2CH_2CH_2I$, 627-31-6; $I(CH_2)_5I$, 628-77-3; PhCHBrMe, 585-71-7; $BrCMe_2CO_2Et$, 600-00-0; $Br(CH_2)_3CO_2Et$, 2969-81-5; $MeCHBrCO_2Me$, 5445-17-0; $MeCHBrCO_2Et$, 535-11-5; $EtCHBrCO_2Me$, 3196-15-4; $EtCHBrCO_2Et$, 533-68-6; $H_3CCH_2CH_2CH_3$, 106-97-8; $CH_2{=}CHCH_2CH_3$, 106-98-9; *cis*-$H_3CCH{=}CHCH_3$, 590-18-1; *trans*-$H_3CCH{=}CHCH_3$, 624-64-6; $CH_2{=}CH(CH_2)_4I$, 18922-04-8; Me_3CCH_2I, 15501-33-4; ICH_2CHMe_2, 513-38-2; $PhCH{=}CH_2$, 100-42-5; PhEt, 100-41-4; $CH_2{=}CMeCO_2Et$, 97-63-2; Me_2CHCO_2Et, 97-62-1; $CH_2{=}CHCO_2Me$, 96-33-3; $EtCO_2Me$, 554-12-1; $MeCH{=}CHCO_2Me$, 18707-60-3; *n*-$PrCO_2Me$, 623-42-7; MePrCHBr, 107-81-3; $PhCH_2CH_2Br$, 103-63-9; $PhCH_2Cl$, 100-44-7; $CH_2{=}CMeCH_2Cl$, 563-47-3; PhBr, 108-86-1.

OM920153Y

Electronic Structure and Reactivity of Carbynyl Cation (CR^+) Bridged Binuclear Transition-Metal Complexes

Eluvathingal D. Jemmis* and Bharatam V. Prasad[†]

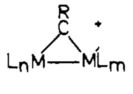
School of Chemistry, University of Hyderabad, Central University P.O., Hyderabad-500 134, India

Received August 2, 1991

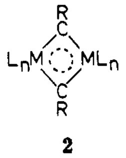
Extended Hückel calculations on carbynyl cation (CR^+) bridged binuclear transition metal complexes show that the reactivity is controlled by the LUMO of these compounds. These compounds fall into two categories according to whether or not the compound is isolobal with the cyclopropyl cation. Complexes such as $(CO)CpFe(\mu\text{-}CH)(\mu\text{-}CO)FeCp(CO)^+$, $Cp(CO)_2Mn(\mu\text{-}CR)PtL_2^+$, and $(CO)_5W(\mu\text{-}CR)PtL_2^+$, which are isolobal to the cyclopropyl cation, have a carbon-based p orbital as the LUMO. They are reactive toward the incoming nucleophiles at the carbon center. On the other hand, cationic complexes such as $CpRh(\mu\text{-}CR)(\mu\text{-}CO)RhCp^+$ and $Cp(CO)_2W(\mu\text{-}CR)AuL^+$ do not have a carbon-based LUMO and are expected to be unreactive toward nucleophiles. A least motion path for the hydrocarbation reaction is studied. Many potential candidates for the hydrocarbation reaction are suggested.

Introduction

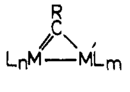
Reactions occurring at bridging hydrocarbyl ligands have been the subject of great interest from both experimental and theoretical points of view because of their potential catalytic activity.[1] The chemistry of the compounds with a carbyne (CR) bridging two transition metals, **1**–**3**, is of special interest[2] as a model for the Fischer–Tropsch synthesis.[2a] Compounds represented by **2** are reactive at the metal center.[2c] Compounds of type **3** are reactive either at the M=C double bond without any loss of ligands or at M′ after the loss of a ligand.[2b] In **2** and **3**, the carbyne is considered as a three-electron donor. But a CR^+ bridge, as in **1**, can contribute only two electrons to the complex formation. These two participate in regular M–C σ bonds.



1

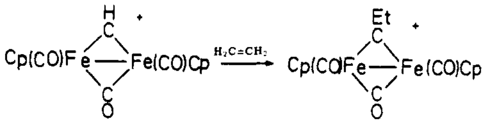


2



3

Scheme I



4 5

The unsaturation at the carbon center, indicated by positive charge, leads to unusual reactivity, and a theoretical study of the system is presented in this paper.

In general, compounds of type **1** are prepared via five different routes: (1) protonating vinylidene-bridged bi-

---

[†] Present address: University of Alabama at Birmingham, UAB Station, Birmingham, AL 35294.

(1) Important reviews dealing with the bridging CR units: (a) Connor, J. A. *Organomet. Chem.* **1976**, *5*, 245. (b) Evans, J. *Annu. Rep. Prof. Chem., Sect. A., Inorg. Chem.* **1979**, *76*, 190. (c) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. W. *Chem. Rev.* **1983**, *83*, 135. (d) Stone, F. G. A. Inorganic Chemistry Towards 21st Century. Chishlom, M. H., Ed. *ACS Symp. Ser.* **1983**, No. *211*, 383. (e) The Chemistry of Bridging Hydrocarbyl Ligands, a Symposium-in-Print. Chisholm, M. H., Ed. *Polyhedron* **1988**, *7*, 757–1052.

(2) (a) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (b) Stone, F. G. A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 89. (c) Jemmis, E. D.; Prasad, B. V. *J. Am. Chem. Soc.* **1987**, *109*, 2560. Prasad, B. V. Ph.D. Thesis, University of Hyderabad. (d) Bruice, M. I. *Chem. Rev.* **1991**, *91*, 197.

0276-7333/92/2311-2528$03.00/0