3588 *Organometallics* **1996,** *15,* 3588−3599

$FvCr_2(CO)_4L_2$ (Fv = Fulvalene; L = PMe_2Ph, PMe_3), Metal−Metal-Bonded Compounds Which Undergo Spontaneous Thermal Homolysis to Their Biradical Isomers. Relevant Chemistry of the Compounds $FvCr_2(CO)_4L_2X_2$ (X = H, Cl, Br, I)

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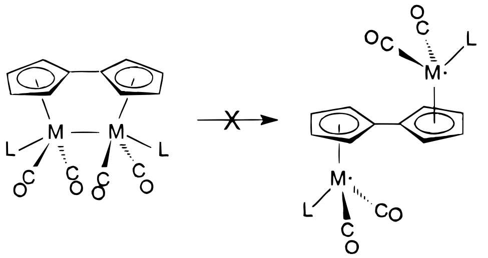
Received January 29, 1996[⊗]

Two new (fulvalene)dichromium carbonyl dihydrides, $FvCr_2(CO)_4L_2H_2$ (L = PMe_2Ph (**2b**), PMe_3 (**2c**)) were prepared by phosphine substitution of $FvCr_2(CO)_6H_2$ (**2a**) and studied by variable-temperature ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR. Compound **2b** assumes a 77:23 and **2c** an 85:15 *cis*/*trans* isomeric ratio at −50 °C, while low-temperature NMR spectra of **2b** present evidence for the *meso* and *dl* forms of the *cis*,*cis* isomer. Hydride hydrogen atom abstraction from **2b** and **2c** by $Ph_3C^\bullet$, as well as hydrogenation of isoprene and 1,3,5-hexatriene by **2b** and **2c**, result in the formation of $FvCr_2(CO)_4L_2$ (L = PMe_2Ph (**6a**), PMe_3 (**6b**)). Variable-temperature IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR studies demonstrate that both **6a** and **6b** maintain facile equilibria between the *trans* isomers of the chromium−chromium-bonded species and the novel biradical species $L(CO)_2Cr(\mu\text{-}Fv)Cr(CO)_2L$ at room temperature in solution. Room-temperature reactions of **6a** with alkyl halides reflect the radical character of this compound, halogen atom abstractions leading to the new dihalide compounds $FvCr_2(CO)_4(PMe_2Ph)_2X_2$ (X = I (**3b**), Br (**4**), Cl (**5**)). Compounds **3b**, **4**, and **5** were obtained alternatively in the hydrogen−halogen atom exchange reactions of **2b** with the appropriate alkyl halides. These reactions are shown to proceed via intermediate formation of the corresponding mixed hydrido halide compounds *cis*-$FvCr_2(CO)_4(PMe_2Ph)_2HX$ (containing *cis*-halide halves). $FvCr_2(CO)_6I_2$ (**3a**) was prepared analogously from **2a** and ethyl iodoacetate and was also identified as the product of iodine atom abstraction from ethyl iodoacetate by $FvCr_2(CO)_6$. The reaction of $FvCr_2(CO)_6I_2$ with PMe_2Ph provided access to *cis*-$(CO)_2(PMe_2Ph)ICr(\mu\text{-}Fv)$[*trans*-$Cr(CO)_2(PMe_2Ph)_2$]I (**7**); the reaction was shown to proceed via consecutive formation of the intermediates $(CO)_3ICr(\mu\text{-}Fv)[Cr(CO)_3PMe_2Ph]I$ and *cis*-$(CO)_2(PMe_2Ph)ICr(\mu\text{-}Fv)[Cr(CO)_3PMe_2Ph]I$.

Introduction

We are currently engaged in an investigation of phosphine-substituted, homobimetallic (fulvalene)dimolybdenum and -dichromium carbonyl complexes of the type *trans*-$FvM_2(CO)_4L_2$ (M = Mo, L = PPh_3, PCy_3 (Cy = cyclohexyl), PXy_3 (Xy = 3,5-dimethylphenyl); M = Cr, L = PMe_2Ph).[1] These compounds are of interest because the parent dimers $FvM_2(CO)_6$ (M = Cr, Mo, W) contain extraordinarily long metal−metal bonds but do not undergo significant thermal metal−metal bond homolysis to their biradical isomers $L(CO)_2M(\mu\text{-}Fv)M(CO)_2L$ (L = CO) (eq 1),[2] in striking contrast with $[CpCr(CO)_3]_2$.[4,5] We hoped to induce the formation of biradical isomers by using bulky ligands, an approach which has proven to be very effective for stabilizing the 17-electron,



(1)

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[⊗] Abstract published in *Advance ACS Abstracts*, July 1, 1996.

[1] (a) Kovács, I.; Baird, M. C. *Organometallics* **1995**, *14*, 4074. (b) Kovács, I.; Baird, M. C. *Organometallics* **1995**, *14*, 4084. (c) Kovács, I.; Baird, M. C. *Organometallics* **1995**, *14*, 5469.

[2] (a) McGovern, P. A.; Vollhardt, K. P. C. *Synlett* **1990**, 493. (b) Note, however, that $FvCr_2(CO)_6$ catalyzes the 1,4-dihydrogenation of conjugated dienes, as does $[CpCr(CO)_3]_2$ via $CpCr(CO)_3$ and $CpCr(CO)_3H$,[3] which can be taken as indirect evidence for the diradical isomer of $FvCr_2(CO)_6$. Vollhardt, K. P. C. Personal communication.

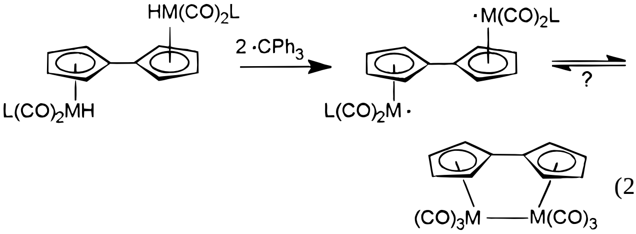
[3] Miyake, A.; Kondo, H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 631.

[4] (a) Baird, M. C. *Chem. Rev.* **1988**, *88*, 1217. (b) Trogler, W. C., Ed. *Organometallic Radical Processes*; J. Organomet. Chem. Library 22; Elsevier: Amsterdam, 1990.

[5] For more recent information, see the following. $CpCr(CO)_3$: (a) Goh, L. Y.; Lim, Y. Y. *J. Organomet. Chem.* **1991**, *402*, 209. (b) Fortier, S.; Baird, M. C.; Preston, K. F.; Morton, J. R.; Ziegler, T.; Jaeger, T. J.; Watkins, W. C.; MacNeil, J. H.; Watson, K. A.; Hensel, K.; LePage, Y.; Charland, J.-P.; Williams, A. J. *J. Am. Chem. Soc.* **1991**, *113*, 542. (c) O'Callaghan, K. A. E.; Brown, S. J.; Page, J. A.; Baird, M. C.; Richards, T. C.; Geiger, W. E. *Organometallics* **1991**, *10*, 3119. (d) Watkins, W. C.; Jaeger, T.; Kidd, C. E.; Fortier, S.; Baird, M. C.; Kiss, G.; Roper, G. C.; Hoff, C. D. *J. Am. Chem. Soc.* **1992**, *114*, 907. (e) MacConnachie, C. A.; Nelson, J. M.; Baird, M. C. *Organometallics* **1992**, *11*, 2521. (f) Yao, Q.; Bakac, A.; Espenson, J. H. *Organometallics* **1993**, *12*, 2010. (g) Richards, T. C.; Geiger, W. E.; Baird, M. C. *Organometallics* **1994**, *13*, 4494. $CpMo(CO)_3$: (h) Pugh, J. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 3784. (i) Scott, S. L.; Espenson, J. H.; Zhu, Z. *J. Am. Chem. Soc.* **1993**, *115*, 1789. $CpW(CO)_3$: Reference 3i and (j) Scott, S. L.; Espenson, J. H.; Bakac, A. *Organometallics* **1993**, *12*, 1044. (k) Scott, S. L.; Espenson, J. H.; Chen, W.-J. *Organometallics* **1993**, *12*, 4077. (l) Zhu, Z.; Espenson, J. H. *Organometallics* **1994**, *13*, 1893.

S0276-7333(96)00051-9 CCC: $12.00

metal-centered radicals $Cp'M(CO)_2L$ (M = Cr, Mo; L = phosphine, phosphite; Cp′ = substituted cyclopentadienyl).[4,5a−d,6] Our general approach to biradical formation has involved the hydrogen atom abstraction reaction of trityl radicals ($Ph_3C^•$)[7] with the corresponding hydrides $FvM_2(CO)_4L_2H_2$ (M = Cr, Mo), as in eq 2.[1]



(2)

We were able to obtain indirect verification of the intermediate formation of metal-centered biradicals, during both the hydrogen atom transfer process from $FvMo_2(CO)_4(PPh_3)_2H_2$ to $Ph_3C^•$ and the light-induced homolytic dissociation of *trans*-$FvMo_2(CO)_4(PPh_3)_2$, by formation of $FvMo_2(CO)_4(PPh_3)_2X_2$ (X = Cl, Br, I), the anticipated products of halogen atom abstraction reactions of the biradicals with alkyl halides.[1a,b] In a preliminary communication we also reported the first direct, variable-temperature IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR evidence for the existence of a facile thermal equilibrium between *trans*-$FvCr_2(CO)_4(PMe_2Ph)_2$ (obtained by hydrogen atom abstraction by $Ph_3C^•$ from $FvCr_2(CO)_4(PMe_2Ph)_2H_2$) and its biradical isomer, $PMe_2Ph(CO)_2Cr(\mu\text{-}Fv)Cr(CO)_2PMe_2Ph$.[1c] The latter undergoes halogen atom abstraction reactions with alkyl halides, and there is thus growing evidence that these phosphine-substituted (fulvalene)molybdenum and chromium carbonyl "dimers" do indeed exhibit dissociative behavior which resembles that of the corresponding Cp complexes.[5a−d,6]

We now report further details of the preparation, spectroscopic properties and reactions of $FvCr_2(CO)_4(PMe_2Ph)_2$ and another derivative, $FvCr_2(CO)_4(PMe_3)_2$. Since direct phosphine substitution of $FvCr_2(CO)_6$ is not a viable route to prepare such complexes,[2a] we utilized the hydride hydrogen atom abstraction reactions of the corresponding dihydrides with trityl radicals; this approach required detailed investigations of the compounds $FvCr_2(CO)_4L_2H_2$ (L = CO, PMe_3, PMe_2Ph) as well. In order to verify radical-like reactivities of $FvCr_2(CO)_4(PMe_2Ph)_2$, we also investigated its reactions with various alkyl halides, and thus the necessity to identify possible products of these reactions required an examination of the corresponding dihalides $FvCr_2(CO)_4L_2X_2$ (L = CO, PMe_2Ph; X = Cl, Br, I). In this context we note that related chromium compounds containing Cp and substituted cyclopentadienyl ligands have only been sporadically studied until recently,[8] probably because of low stabilities which make them difficult to handle. Relevant data for comparison with (fulvalene)chromium compounds are even more limited, unlike the situation with the much more robust molybdenum and tungsten analogues. Most of the compounds reported in this article are new.[9]

Table 1. Carbonyl Stretching Frequences

compd	ν_{CO} (cm^{-1})
$(Et_4N)_2[FvCr_2(CO)_6]$ (**1**)	1890 (vs), 1800 (vs), 1717 (s)[a]
$FvCr_2(CO)_6H_2$ (**2a**)	2008 (vs), 1936 (vs, sh), 1929 (vs)[b]
$FvCr_2(CO)_4(PMe_2Ph)_2H_2$ (**2b**)	1924.5 (vs), 1856 (vs), 1846 (sh)[b]
$FvCr_2(CO)_4(PMe_3)_2H_2$ (**2c**)	1921 (vs), 1853 (s)[c]
$FvCr_2(CO)_6I_2$ (**3a**)	2026 (s), 1972 (vs), 1951 (s, br)[a]
cis,cis-$FvCr_2(CO)_4(PMe_2Ph)_2I_2$ (**3b**)	1958 (vs), 1877 (m, br)[b]
cis,cis-$FvCr_2(CO)_4(PMe_2Ph)_2Br_2$ (**4**)	1968 (vs), 1881 (m)[d]
trans,trans-$FvCr_2(CO)_4(PMe_2Ph)_2Br_2$ (**4**)	1954 (m), 1881 (vs)[d]
cis,cis-$FvCr_2(CO)_4(PMe_2Ph)_2Cl_2$ (**5**)	1973 (vs), 1881 (m)[d]
trans,trans-$FvCr_2(CO)_4(PMe_2Ph)_2Cl_2$ (**5**)	1954 (m), 1881 (vs)[d]
$FvCr_2(CO)_4(PMe_2Ph)_2$ (**6a**)	1926 (s), 1850 (vs)[b]
$FvCr_2(CO)_4(PMe_3)_2$ (**6b**)	1923 (m-s), 1846 (vs)[c]
cis-$PMe_2Ph(CO)_2ICr(\mu\text{-}Fv)$[*trans*-$Cr(CO)_2(PMe_2Ph)_2$]I (**7**)	1956 (vs), 1878 (vs)

[a] In THF. [b] In toluene. [c] In benzene. [d] In CH_2Cl_2.

Experimental Section

General Considerations. All manipulations were carried out under purified nitrogen by using standard Schlenk techniques and a Vacuum Atmospheres glovebox. All solvents were freshly distilled under nitrogen from sodium benzophenone ketyl except CH_2Cl_2, which was distilled from CaH_2. Deuterated solvents were purchased from CDN Isotopes and CIL and were degassed and stored in the glovebox. Alkyl halides, PMe_3, PMe_2Ph, 1,3,5-hexatriene, and isoprene were purchased from Aldrich and used as received, while trityl dimer was prepared as previously reported.[6c] IR spectra were recorded on a Bruker IFS 25 FT-IR spectrometer using a 0.2 mm NaCl cell; for variable-temperature IR studies, the cell temperature was controlled by a Fenwall Model 550 thermocouple. UV−visible spectra were run on a Hewlett-Packard 8452A diode array spectrophotometer and NMR spectra on Bruker AC-200 (200.1 MHz, ^1H) and AM-400 (400.1 MHz, ^1H; 100.6 MHz, $^{13}C\{^1H\}$; 162.0 MHz, $^{31}P\{^1H\}$) NMR spectrometers. IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR data are listed in Tables 1−4, respectively. EI- and FAB(+)-MS analyses were carried out on a Fisons VG Quattro triple quadrupole mass spectrometer, the latter using 3-nitrobenzyl alcohol as the matrix. High-resolution FAB(+) mass spectra were obtained on a Fisons AutoSpec instrument. Elemental analyses were carried out by Canadian Microanalytical Services Ltd. (Delta, BC, Canada).

$(Et_4N)_2[FvCr_2(CO)_6]$ (1). This compound was previously synthesized by Vollhardt et al.,[12] but little information was provided. In our procedure, a solution of $Li_2C_{10}H_8$ (~15 mmol) in 135 mL of THF/hexane (8:1)[1a] was added by syringe to a mixture of $Cr(CO)_3(EtCN)_3$ (9.0 g, 30 mmol) and Et_4NBr (6.3 g, 30 mmol). The yellow-brown slurry was refluxed for 1 h, and at this point an IR spectrum of the reaction mixture showed complete consumption of the starting chromium complex and formation of the expected anionic product. Most of the solvent was evaporated under reduced pressure, and

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(6) See also the following. $CpCr(CO)_2L$: (a) Cooley, N. A.; MacConnachie, P. T. F.; Baird, M. C. *Polyhedron* **1988**, *7*, 1965. (b) Watkins, W. C.; Hensel, K.; Fortier, S.; Macartney, D. H.; Baird, M. C.; McLain, S. J. *Organometallics* **1992**, *11*, 2418. $CpMo(CO)_2PPh_3$: (c) Drake, P. R.; Baird, M. C. *J. Organomet. Chem.* **1989**, *363*, 131. $CpW(CO)_2PPh_3$: Reference 5k.

(7) (a) Koeslag, M. D.; Baird, M. C. *Organometallics* **1994**, *13*, 11. (b) Kuksis, I.; Baird, M. C. *Organometallics* **1994**, *13*, 1551. (c) Eisenberg, D. C.; Lawrie, C. J. C.; Moody, A. E.; Norton, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 4888. (d) Eisenberg, D. C.; Norton, J. R. *Isr. J. Chem.* **1991**, *31*, 55 and references therein.

(8) Davis, R.; Kane-Maguire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 3, p 953.

(9) In fact, the only well-characterized (fulvalene)dichromium carbonyl complex reported so far is the chromium−chromium-bonded dimer $FvCr_2(CO)_6$.[2a,10,11] $FvCr_2(CO)_6I_2$ has also been mentioned in the literature but not characterized,[11] and we have been informed that $(Et_4N)_2[FvCr_2(CO)_6]$, $FvCr_2(CO)_6H_2$, and $FvCr_2(CO)_6Me_2$ were studied previously by Vollhardt et al.[12]

(10) Vollhardt, K. P. C.; Weidman, T. W. *Organometallics* **1984**, *3*, 82.

(11) Moulton, R.; Weidman, T. W.; Vollhardt, K. P. C.; Bard, A. J. *Inorg. Chem.* **1986**, *25*, 1846.

(12) McGovern, P. A.; Vollhardt, K. P. C. Private communication.

Table 2. ^{1}H NMR Data

	^{1}H chem shifts (δ, 25 °C)	
compd	fulvalene	other
$(Et_4N)_2[FvCr_2(CO)_6]$ (**1**)[a]	4.13 (“t”, 4H), 4.61 (“t”, 4H)	1.36 (tt, $J_1 = 7$ Hz, $J_2 = 2$ Hz, 24H, Me), 3.42 (q, $J = 7$ Hz, 16H, CH_2N)
$FvCr_2(CO)_6H_2$ (**2a**)[b]	4.08 (“t”, 4H), 4.34 (“t”, 4H)	−5.46 (s, 2H, CrH)
$FvCr_2(CO)_4(PMe_2Ph)_2H_2$ (**2b**)[b]	4.04 (“q”, 4H), 4.35 (“q”, 4H)	−6.07 (d, $J_{PH} = 73$ Hz, 2H, CrH), 1.26 (d, $J_{PH} = 8$ Hz, 12H, PMe), ~7.06 (m, 6H, *m*, *p*-Ph), 7.30 (“t”, 4H, *o*-Ph)
$FvCr_2(CO)_4(PMe_3)_2H_2$ (**2c**)[b]	4.13 (“q”, 4H), 4.57 (“q”, 4H)	−6.45 (d, $J_{PH} = 81$ Hz, 2H, CrH), 0.98 (d, $J_{PH} = 9$ Hz, 18H, PMe)
$FvCr_2(CO)_6I_2$ (**3a**)[a]	5.54 (“t”, 4H), 5.90 (“t”, 4H)	
$FvCr_2(CO)_4(PMe_2Ph)_2HCl$[c]	4.38 (m, 3H), 4.44, 4.50, 4.61, 4.74, 5.20 (all m, 1H)	
$FvCr_2(CO)_4(PMe_2Ph)_2HBr$[b]	3.92, 4.00, 4.04, 4.06, 4.27, 4.46, 4.62, 4.93 (all m, 1H)	
$FvCr_2(CO)_4(PMe_2Ph)_2HI$[b]	3.90 (m, 2H), 4.02, 4.04, 4.27, 4.53, 4.67, 4.86 (all m, 1H)	
$FvCr_2(CO)_4(PMe_2Ph)_2I_2$ (*cis*,*cis*-**3b**)[b]	3.70, 3.81, 3.92, 4.23, 4.42, 4.49, 4.84, 5.29 (all m, 1H)	1.63 (d, $J_{PH} = 8$ Hz, 3H, PMe), 1.65 (d, $J_{PH} = 8$ Hz, 3H, PMe), 1.68 (d, $J_{PH} = 9$ Hz, 3H, PMe), 1.69 (d, $J_{PH} = 9$ Hz, 3H, PMe), ~7.10 (m, 6H, *m*,*p*-Ph), 7.33 ("t", 4H, *o*-Ph)
$FvCr_2(CO)_4(PMe_2Ph)_2Br_2$ (*cis*,*cis*-**4**)[b]	3.70, 3.83, 4.00, 4.21, 4.85, 5.19 (all m, 1H), 4.38 (m, 2H)	1.53 (br m, 18H, PMe), ~7.08 (m, 6H, *m*,*p*-Ph), 7.39 (m, 4H, *o*-Ph)
$FvCr_2(CO)_4(PMe_2Ph)_2Cl_2$ (*cis*,*cis*-**5**)[c]	4.37, 4.43, 4.50, 4.54 (all m, 1H), 4.73, 5.25 (both m, 2H)	1.85 (br m, 18H, PMe)
$FvCr_2(CO)_4(PMe_2Ph)_2Cl_2$ (*trans*,*trans*-**5**)[c]	3.91, 3.96 (both m, 4H)	1.99 (d, $J_{PH} = 8$ Hz, 18H, PMe)
$FvCr_2(CO)_4(PMe_2Ph)_2$ (**6a**)[b]	3.69 (br m, 4H), 3.92 (br m, 4H)	1.68 (br s, 12H, PMe), ~7.05 (br m, 4H, Ph), 7.41 (br m, 6H, Ph)
$FvCr_2(CO)_4(PMe_3)_2$ (**6b**)[b]	3.87 (m, 4H), 3.90 (m, 4H)	1.21 (br d, 18H, PMe)
cis-$(PMe_2Ph)(CO)_2ICr(\mu\text{-}Fv)$-[*trans*-$Cr(CO)_2(PMe_2Ph)_2]I$ (**7**)[d]	4.71, 4.74, 4.82, 4.95, 5.26, 5.28, 5.33, 5.40 (all m, 1H)	1.96 (d, $J_{PH} = 9$ Hz, 3H, PMe of neutral Cr), 2.02 (m, 12H, PMe of Cr^+), 2.15 (d, $J_{PH} = 9$ Hz, 3H, PMe of neutral Cr), 7.42−7.61 (m, 15H, Ph)
$[(CO)_3ICr](\mu\text{-}Fv)[Cr(CO)_3PMe_2Ph]I$[a]	5.45, 5.91, 6.12, 6.44 (all m, 2H)	2.44 (d, $J_{PH} = 11$ Hz, 6H, PMe), 7.64 (m, 3H, *m*, *p*-Ph), 7.91 (m, 2H, *o*-Ph)
cis-$[PMe_2Ph(CO)_2ICr]$-$(\mu\text{-}Fv)[Cr(CO)_3PMe_2Ph]I$[a]	4.96, 5.13, 5.54, 5.81, 5.85, 6.04, 6.26, 6.38 (all m, 1H)	2.17 (d, $J_{PH} = 9$ Hz, 3H, PMe), 2.26 (d, $J_{PH} = 9$ Hz, 3H, PMe), 2.42 (d, $J_{PH} = 11$ Hz, 3H, PMe), 2.43 (d, $J_{PH} = 11$ Hz, 3H, PMe), 7.42 (m, 3H, *m*,*p*-Ph), 7.63 (m, 3H, *m*,*p*-Ph), 7.78 (m, 2H, *o*-Ph), 7.90 (m, 2H, *o*-Ph)

[a] Acetone-d_6. [b] Toluene-d_8. [c] $CDCl_3$. [d] DMSO-d_6.

Table 3. $^{13}C\{^{1}H\}$ NMR Data

	^{13}C chem shifts (δ, 25 °C)	
compound	fulvalene	other
$(Et_4N)_2[FvCr_2(CO)_6]$ (**1**)[a]	80.0, 81.7, 100.9 (C-1)	7.7 (Me), 52.8 (CH_2N), 247.4 (CO)
$FvCr_2(CO)_6H_2$ (**2a**)[b]	83.7, 85.9, 99.8 (C-1)	234.7 (br, CO)
$FvCr_2(CO)_4(PMe_2Ph)_2H_2$ (**2b**)[c]	83.7, 84.8, 99.9 (C-1)	128.5 (d, $J_{PC} = 8.5$ Hz, Ph), 129.2 (s, Ph), 129.6 (d, $J_{PC} = 9$ Hz, Ph), 143.0 (d, $J_{PC} = 36$ Hz, Ph)
$FvCr_2(CO)_4(PMe_3)_2H_2$ (**2c**)[c]	83.0, 84.2, 100.0 (C-1)	
$FvCr_2(CO)_6I_2$ (**3a**)[d]	91.2, 92.1, 103.2 (C-1)	235.9 (s, CO cis to I), 247.5 (s, CO trans to I)
$FvCr_2(CO)_4(PMe_2Ph)_2I_2$ (**3b**)[d]	83.8, 84.0, 89.2, 89.6, 92.1, 92.9, 95.3, 95.4, 101.8 (C-1), 102.0 (C-1)	19.3 (d, $J_{PC} = 30$ Hz, PMe), 20.38 (d, $J_{PC} = 28$ Hz, PMe), 20.43 (d, $J_{PC} = 28$ Hz, PMe), 127.8 (d, $J_{PC} = 10$ Hz, Ph), 129.6 (s, Ph), 131.6 (d, $J_{PC} = 8$ Hz, Ph), 137.4 (d, $J_{PC} = 44$ Hz, Ph), 252.2 (d, $J_{PC} = 6.5$ Hz, CO cis to I), 260.0 (d, $J_{PC} = 57$ Hz, CO trans to I)
$FvCr_2(CO)_4(PMe_2Ph)_2$ (**6a**)[a]	82.6, 88.4	129.3, 130.0, 130.6 (Ph)
$FvCr_2(CO)_4(PMe_3)_2$ (**6b**)[c]	81.8, 85.1, 87.3 (C-1)	253.6 (d, $J_{PC} = 45$ Hz, CO)
cis-$(PMe_2Ph)(CO)_2ICr(\mu\text{-}Fv)$-[*trans*-$Cr(CO)_2(PMe_2Ph)_2]I$ (**7**)[d]	83.0, 88.9, 89.0, 89.2, 89.7, 90.0, 92.2, 96.9, 98.4 (C-1), 102.8 (C-1)	17.6 (m, PMe of Cr^+), 19.4 (d, $J_{PC} = 30$ Hz, PMe of neutral Cr), 20.6 (d, $J_{PC} = 30$ Hz, PMe of neutral Cr), 127.8 (d, $J_{PC} = 10$ Hz, Ph of neutral Cr), 128.7 (m, Ph of Cr^+), 129.1 (br s, Ph of Cr^+), 129.8 (s, Ph of neutral Cr), 130.6 (s, Ph of Cr^+), 131.6 (d, $J_{PC} = 8$ Hz, Ph of neutral Cr), 136.8 (d, $J_{PC} = 46$ Hz, Ph of Cr^+), 137.0 (d, $J_{PC} = 43$ Hz, Ph of neutral Cr), 245.8 (t, $J_{PC} = 50$ Hz, CO of Cr^+), 251.4 (d, $J_{PC} = 7$ Hz, CO cis to I), 259.3 (d, $J_{PC} = 55$ Hz, CO trans to I)

[a] Acetone-d_6. [b] C_6D_6. [c] Toluene-d_8. [d] DMSO-d_6.

the remaining oil was shaken with 100 mL of hexane to give a yellow gum. After the liquid phase was decanted, the sticky material was dried under reduced pressure. It was then washed with 50 mL portions of ether until colorless washings were obtained, and the resulting yellow solid was thoroughly dried again to yield ~18 g of air-sensitive, impure $(Et_4N)_2[FvCr_2(CO)_6]$. This product contained insoluble byproduct (LiBr) which could be separated, if necessary, by extraction with THF followed by precipitation with hexane; traces of THF and ether could not be completely removed. However, both impure and purified products were satisfactory starting materials for further syntheses.

$FvCr_2(CO)_6H_2$ (2a). Compound **2a** was typically generated *in situ* from 2.0 g of impure $(Et_4N)_2[FvCr_2(CO)_6]$ (containing ~1.62 mmol of the dianion) and 0.6 mL of glacial acetic acid in 75 mL of toluene at room temperature. The dark yellow toluene solution was filtered into another flask, diluted with 25 mL of hexane, and used immediately.

Reaction of 2a with Isoprene. A 0.6 mL acetone-d_6 solution of **1** (10 mg, 1.5×10^{-3} mmol) was treated with a drop of glacial acetic acid to generate hydride **2a**, and a ^{1}H NMR spectrum was recorded. Into this solution was injected 10 μL (0.1 mmol) of isoprene at room temperature, resulting in rapid darkening of the solution and complete transformation of **2a**

Table 4. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR Data

compd	δ (ppm)
$\mathrm{FvCr_2(CO)_4(PMe_2Ph)_2H_2}$ (**2b**)	60.2[a]
$\mathrm{FvCr_2(CO)_4(PMe_2Ph)_2H_2}$ (**2b**)	61.2 (br), 61.3 (br)[a,b]
$\mathrm{FvCr_2(CO)_4(PMe_3)_2H_2}$ (**2c**)	48.2[c]
$\mathrm{FvCr_2(CO)_4(PMe_3)_2H_2}$ (**2c**)	48.80, 48.84 (both *cis*,*cis*), 48.9 (*cis*,*trans*), 49.05 (*cis*,*cis*), 50.64 (*cis*,*trans*), 50.69 (*trans*,*trans*)[b,c]
cis-$\mathrm{FvCr_2(CO)_4(PMe_2Ph)_2HI}$	31.4, 59.1 (br)[c]
cis,*cis*-$\mathrm{FvCr_2(CO)_4(PMe_2Ph)_2I_2}$ (**3b**)	31.15, 31.20;[c] 33.17, 33.20[a]
cis-$\mathrm{FvCr_2(CO)_4(PMe_2Ph)_2HBr}$	35.5, 59.0[d]
cis,*cis*-$\mathrm{FvCr_2(CO)_4(PMe_2Ph)_2Br_2}$ (**4**)	35.2;[d] 35.16, 35.25;[c] 37.4[a]
cis-$\mathrm{FvCr_2(CO)_4(PMe_2Ph)_2HCl}$	39.4, 59.1[d]
cis,*cis*-$\mathrm{FvCr_2(CO)_4(PMe_2Ph)_2Cl_2}$ (**5**)	39.6[d]
trans,*trans*-$\mathrm{FvCr_2(CO)_4(PMe_2Ph)_2Cl_2}$ (**5**)	62.8[d]
trans-$\mathrm{FvCr_2(CO)_4(PMe_2Ph)_2}$ (**6a**)	66.0[b,c]
trans-$\mathrm{FvCr_2(CO)_4(PMe_3)_2}$ (**6b**)	57.4[b,c]
cis-$\mathrm{PMe_2Ph(CO)_2ICr(\mu\text{-}Fv)}$[*trans*-$\mathrm{Cr(CO)_2(PMe_2Ph)_2}$]I (**7**)	32.9 (1P), 51.1 (2P)
cis-$\mathrm{PMe_2Ph(CO)_2ICr(\mu\text{-}Fv)[Cr(CO)_3PMe_2Ph]I}$	32.7 (1P), 42.0 (1P)
cis-$\mathrm{FvCr_2(CO)_5(PMe_2Ph)I_2}$	33.0
$\mathrm{(CO)_3ICr(\mu\text{-}Fv)[Cr(CO)_3PMe_2Ph]I}$	41.7

[a] In acetone-d_6. [b] At −50 °C. [c] In toluene-d_8. [d] In $\mathrm{CDCl_3}$.

into $\mathrm{FvCr_2(CO)_6}$, identified by a second ^{1}H NMR spectrum, which exhibited resonances identical with those previously reported.[10] IR (THF): ν_{CO} 2013 (s), 1951 (vs), 1933 (s), 1911 (sh), 1890 (sh) cm^{-1}. (Lit.[10] IR (KBr): 2000 (s), 1920 (vs), 1900 (vs) cm^{-1}.) ^{1}H NMR (acetone-d_6): δ 4.53 ("t", 4H, Fv), 5.24 ("t", 4H, Fv). (Lit.[10] ^{1}H NMR: δ 4.54, 5.25.) $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (acetone-d_6): δ 84.5 (s, Fv), 88.3 (s, Fv), 92.1 (s, C-1 Fv). No CO carbon resonance could be identified.

$\mathrm{FvCr_2(CO)_4(PMe_2Ph)_2H_2}$ (2b). To a stirred solution of **2a**, prepared as described above, was added 0.80 mL of $\mathrm{PMe_2Ph}$ (5.6 mmol), resulting in gas evolution and slow formation of a yellow precipitate (1 day). When no more **2a** was present in the reaction mixture (IR), the supernatant solution was separated, concentrated under reduced pressure to ∼5 mL, and diluted with 20 mL of hexane to give a second crop of solid material. The combined precipitates were washed with 3 × 10 mL of hexane and dried under reduced pressure to yield 0.74 g (1.19 mmol, 73% based on $\mathrm{Cr(CO)_3(EtCN)_3}$) of a yellow powder, which was recrystallized from a 2:1 THF−hexane solvent mixture. Complex **2b** was indefinitely stable in the solid state but slowly decomposed in solution to an unidentified green precipitate. It is soluble in many aromatic and polar solvents. Anal. Calcd for $\mathrm{C_{30}H_{32}Cr_2O_4P_2}$: C, 57.88; H, 5.18. Found: C, 57.30, H, 5.33. High-resolution FAB(+)-MS: m/z 621.050 089, calcd for $[\mathrm{M-H}]^+$ 621.050 781. EI-MS: m/z (%) (no $[\mathrm{M}]^+$ appeared) $[\mathrm{M-2H-CO}]^+ = 592$ (0.2), $[\mathrm{M-2H-2CO}]^+ = 564$ (0.8), $[\mathrm{M-2H-3CO}]^+ = 538$ (2.2), $[\mathrm{M-2H-4CO}]^+ = 508$ (0.5), $[\mathrm{M-2H-PMe_2Ph}]^+ = 482$ (0.4), $[\mathrm{M-2H-PMe_2Ph-CO}]^+ = 454$ (0.2), $[\mathrm{M-2H-PMe_2Ph-2CO}]^+ = 426$ (0.2), $[\mathrm{M-2H-PMe_2Ph-3CO}]^+ = 398$ (0.2), $[\mathrm{M-2H-PMe_2Ph-4CO}]^+ = 370$ (3.3), $[\mathrm{FvCrH}]^+ = 181$ (11), $[\mathrm{Fv}]^+ = 128$ (33). ^{1}H NMR (toluene-d_8, −50 °C): δ −6.43 (d, J_{PH} = 89 Hz, CrH, *cis*), −6.39 (d, J_{PH} = 89 Hz, CrH, *cis*), −5.43 (d, J_{PH} = 26 Hz, CrH, *trans*), 1.06 (br s, PMe), 1.20 (br s, PMe), 3.94−4.23 (br m, Fv), 7.01 (br s, Ph). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (toluene-d_8, 25 °C): δ 83.7 (s, Fv), 84.8 (s, Fv), 99.9 (s, C-1 Fv), 128.5 (d, J_{PC} = 8.5 Hz, *m*-Ph), 129.2 (s, *p*-Ph), 129.6 (d, J_{PC} = 9 Hz, *o*-Ph), 143.0 (d, J_{PC} = 36 Hz, *ipso*-Ph) (no CO or PMe resonances were observed). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (acetone-d_6, −60 °C): δ 21.8 (d, J_{PC} = 31 Hz, PMe), 22.5 (br d, J_{PC} = 33 Hz, PMe), 82.6, 83.4, 84.3, 85.5, 85.7, 85.9 (s, all Fv), 100.0, 100.5 (s, both C-1 Fv), 128.9 (d, J_{PC} = 8 Hz, *m*-Ph), 129.7 (s, *p*-Ph), 130.1 (d, J_{PC} = 8 Hz, *o*-Ph), 142.5 (d, J_{PC} = 42 Hz, *ipso*-Ph), 243.7 (d, J_{PC} = 6.5 Hz, CO cis to H), 251.4 (d, J_{PC} = 42 Hz, CO trans to H).

$\mathrm{FvCr_2(CO)_4(PMe_3)_2H_2}$ (2c). Compound **2c** was obtained as an olive green solid by adding 0.7 mL of $\mathrm{PMe_3}$ (6.8 mmol) to a solution of **2a**. Yield: 0.50 g (1.00 mmol, 62% based on $\mathrm{Cr(CO)_3(EtCN)_3}$). It was found to be more soluble in common organic solvents and less stable than **2b**, and thus recrystallization resulted in substantial loss and an analytically pure sample could not be isolated. The compound was therefore characterized spectroscopically. High-resolution FAB(+)-MS: m/z 497.017 167, calcd for $[\mathrm{M-H}]^+$ 497.016 428. EI-MS: m/z (%) (no $[\mathrm{M}]^+$ appeared) $[\mathrm{M-2H}]^+ = 496$ (2.8), $[\mathrm{M-2H-2CO}]^+ = 440$ (7.2), $[\mathrm{M-2H-4CO}]^+ = 384$ (4.4), $[\mathrm{M-2H-PMe_3-3CO}]^+ = 336$ (3.9), $[\mathrm{M-2H-2PMe_3-CO}]^+ = 316$ (3.4), $[\mathrm{M-2H-PMe_3-4CO}]^+ = 308$ (13.4), $[\mathrm{M-2H-2PMe_3-2CO}]^+ = 288$ (3.6), $[\mathrm{M-2H-2PMe_3-3CO}]^+ = 260$ (21.0), $[\mathrm{M-2H-2PMe_3-4CO}]^+ = 232$ (3.8), $[\mathrm{FvCr}]^+ = 180$ (15.5), $[\mathrm{Fv}]^+ = 128$ (100), $[\mathrm{O{=}PMe_3}]^+ = 92$ (21.0), $[\mathrm{PMe_3}]^+ = 76$ (61.3). ^{1}H NMR (toluene-d_8, −50 °C): δ −6.82 (d, J_{PH} = 93 Hz, CrH, *cis*), −6.77 (d, J_{PH} = 92 Hz, CrH, *cis*), −5.53 (d, J_{PH} = 28 Hz, CrH, *trans*), 0.85 (br d, PMe), 4.09−4.54 (br m, Fv). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (toluene-d_8, 25 °C): δ 83.0 (s, Fv), 84.2 (s, Fv), 100.0 (s, C-1 Fv). No CO or PMe resonances were observed.

$\mathrm{FvCr_2(CO)_6I_2}$ (3a). This compound was prepared previously by iodine cleavage of $\mathrm{FvCr_2(CO)_6}$, but no experimental data were given.[11] We have developed alternative methods of preparation, as follows. Into a vigorously stirred solution of **2a**, prepared as above, were injected 2 mL (16.9 mmol) of ethyl iodoacetate, and stirring was continued for 3 h in the dark. The reaction mixture was then decanted to leave a fine solid, which was washed with 3 × 10 mL of hexane and dried under reduced pressure. Yield: 0.67 g (1.02 mmol, 63% based on $\mathrm{Cr(CO)_3(EtCN)_3}$). Compound **3a** is a light-sensitive, rust brown solid which is poorly soluble in nonpolar organic solvents. It was stored at −20 °C in the dark. Anal. Calcd for $\mathrm{C_{16}H_8Cr_2I_2O_6}$: C, 29.38; H, 1.23. Found: C, 29.95; H, 1.48.

Formation of ethyl acetate was verified by NMR spectroscopy when the reaction of **2a** with excess ethyl iodoacetate was carried out in toluene-d_8. ^{1}H NMR of ethyl acetate: δ 0.95 (t, J_{HH} = 7 Hz, 3H, *Me*CH$_2$), 1.65 (s, 3H, *Me*CO), 3.88 (q, J_{HH} = 7 Hz, 2H, CH$_2$). While the fulvalene resonances of **3a** were observed at δ 4.14 ("t", 4H) and 4.41 ("t", 4H), this compound quickly precipitated from solution. The anticipated intermediate $\mathrm{FvCr_2(CO)_6HI}$ was not detected.

Compound **3a** was also prepared by treating 0.02 g (0.05 mmol) of $\mathrm{FvCr_2(CO)_6}$ in 10 mL of THF with 20 μL (0.16 mmol) of ethyl iodoacetate at room temperature. The mixture was stirred under fluorescent lights, and IR spectroscopic monitoring showed slow transformation of the starting dimer to **3a** as the sole carbonyl-containing product. The reaction was complete in ∼1 day. No attempt was made to isolate **3a** from this mixture.

$\mathrm{FvCr_2(CO)_4(PMe_2Ph)_2HX}$ (X = Cl, Br, I). Reactions of **2b** with ∼10-fold excesses of $\mathrm{CCl_4}$, $\mathrm{CHBr_3}$, or $\mathrm{ICH_2CO_2Et}$ were carried out at room temperature with NMR-scale samples containing ∼5 mg (8.0×10^{-3} mmol) of **2b** dissolved in 0.6 mL of toluene-d_8 or $\mathrm{CDCl_3}$ and 10 μL of alkyl halide. Transient formation of the hydrido halide intermediates $\mathrm{FvCr_2(CO)_4(PMe_2Ph)_2HX}$ (X = I, Br, Cl, respectively) was detected *in situ* by ^{1}H NMR spectroscopy in the characteristic fulvalene proton region (the CrH, PMe, and Ph resonances extensively overlapped with those of **2b** and the product dihalides). The identity of these intermediates was supported by the transient $^{31}P\{^1H\}$ NMR spectra, which featured two singlet resonances of equal intensity in the upfield halide and downfield hydride region,[1a,b] both being different from the resonances of **2b** and the corresponding dihalide. The mixed hydrido halides were found to readily react further with the alkyl halides to give the expected dihalo complexes $FvCr_2(CO)_4(PMe_2Ph)_2X_2$ (X = I (**3b**), Br (**4**), Cl (**5**)) and completely disappeared after ~1 h. When less reactive alkyl halides such as *t*-BuI and BzBr were used, the intermediates remained longer, but their formation from **2b** was also slow and the reactions were difficult to monitor because of decomposition and precipitation of the unstable and poorly soluble dihalides. In view of the transient nature of the hydrido halides, they could not be isolated and further characterized.

$FvCr_2(CO)_4(PMe_2Ph)_2X_2$ (X = I (3b), Br (4), Cl (5)). The dibromide compound **4** and dichloride **5** proved to be very unstable at room temperature and under ambient light and were therefore characterized only *in situ* by ^1H and $^{31}P\{^1H\}$ NMR and IR spectroscopy. In contrast, **3b** was isolated in analytically pure form as the *cis,cis* isomer and characterized spectroscopically. Thus, data for *cis,cis*-**3b** were used for comparisons to support the identities of the less stable analogs **4** and **5**.

Compound **3b** was isolated as a purple-brown microcrystalline solid from the reaction of **2b** (0.30 g, 0.47 mmol) with 1.5 mL (12.7 mmol) of ethyl iodoacetate in 30 mL of toluene at room temperature and in the dark for 4 h. After the liquid phase had been removed by syringe, the solid product was washed with 3 × 10 mL of hexane and dried under reduced pressure, yielding 0.33 g (79%) of *cis,cis*-**3b**. It is soluble only in THF and is light-sensitive even in the solid state, although it can be stored in the dark at −20 °C without considerable degradation. Anal. Calcd for $C_{30}H_{30}Cr_2I_2O_4P_2$: C, 41.21; H, 3.46. Found: C, 40.93; H, 3.48. Compound **3b** was also formed in an NMR-scale experiment by adding a solution of I_2 in toluene-d_8 dropwise to ~5 mg (8.0×10^{-3} mmol) of **2b** dissolved in 0.6 mL of toluene-d_8. ^1H NMR spectra of the reaction mixture showed instant formation of a mixture of $FvCr_2(CO)_4(PMe_2Ph)_2HI$ and **3b** with less than 2 molar equiv of iodine, while **3b** was the sole product when the reaction was completed.

For IR spectroscopic characterization, 10 mg (1.6×10^{-2} mmol) of **2b** was dissolved in 2 mL of CH_2Cl_2, a ~20-fold excess of CCl_4, $CHBr_3$, or ICH_2CO_2Et was added at room temperature and in the dark, and the spectra were recorded after ~0.5 h; only absorbances of the dihalides were observed.

The hydrogen−halogen exchange reaction of **2c** (~5 mg, 0.01 mmol) with 10 μL (0.11 mmol) of $CHBr_3$ was briefly investigated, $FvCr_2(CO)_4(PMe_3)_2Br_2$ being obtained. IR (CH_2Cl_2): 1967 (vs, br), 1877 (vs) cm^{-1}. ^1H NMR of the *cis,cis* isomer (toluene-d_8): δ 1.17 (br d, J_{PH} = 9 Hz, 18H, PMe), 3.79, 3.85, 4.16, 4.29, 4.33, 4.36, 4.89, 5.19 (m, 1H, all Fv).

$FvCr_2(CO)_4L_2$ (L = PMe_2Ph (6a), PMe_3 (6b)). These compounds were investigated only in solution, since all attempts to isolate them resulted in extensive decomposition to unidentified species, as indicated by color changes to greenish brown, formation of insoluble precipitates, and broadening of the ^1H NMR resonances. For IR spectroscopic studies, typically 0.02 mmol of the corresponding dihydride (**2b**, **2c**) was dissolved in 3 mL of benzene or toluene and the solution treated with an equivalent amount of the trityl dimer (0.1 M solution in the same solvents) in the dark. The reaction mixtures changed color from yellow to yellow-brown in a few seconds, and IR analyses performed after ~15 min indicated complete consumption of the starting materials and formation solely of the products.

Variable-temperature IR spectroscopic studies carried out on **6a** in the temperature range 25−80 °C showed a decrease of the absorbances of **6a** and formation of a new species (ν_{CO} 1949, 1800 (br) cm^{-1}) as the temperature increased. Unfortunately, the compound decomposed extensively during the experiment, particularly above 50 °C, and no quantitative information could be acquired, although the conversion was clearly shown to be reversible. Decomposition could be due to the thermal sensitivity of **6a** or its radical isomer but might be facilitated by a reaction between the radicals and the cell window (NaCl) as well. It has been mentioned previously that $CpCr(CO)_3$ radicals react with CaF_2 windows.[5d]

For multinuclear NMR studies, typically 0.02 mmol of each of the starting hydrides was dissolved in 0.6 mL of toluene-d_8 or acetone-d_6 and a previously prepared solution of the trityl dimer in the appropriate solvent was added dropwise by microsyringe. Completion of the reactions was monitored by ^1H NMR spectroscopy, which showed formation of **6a** and **6b** as the sole fulvalene compounds formed, along with 2 molar equiv of Ph_3CH (δ 5.37 (CH)); no unreacted trityl dimer remained. NMR data for **6a**: $^{13}C\{^1H\}$ NMR (acetone-d_6, 25 °C) δ 82.6 (s, Fv), 88.4 (s, Fv), 129.3, 130.0, 130.6 (all s, Ph) (no quaternary and PMe carbon resonances appeared); $^{13}C\{^1H\}$ NMR (acetone-d_6, −50 °C) δ 18.7 (d, J_{PC} = 32 Hz, PMe), 82.5 (s, Fv), δ 87.3 (s, C-1 Fv), 88.1 (s, Fv), 129.0, 129.7, 129.8 (s, all Ph), 143.8 (d, J_{PC} = 33.5 Hz, *ipso*-Ph), 254.8 (d, J_{PC} = 35 Hz, CO). $^{13}C\{^1H\}$ NMR for **6b** (toluene-d_8, 25 °C): δ 81.8 (s, Fv), 85.1 (s, Fv), 87.3 (s, C-1 Fv), 253.6 (d, J_{PC} = 45 Hz, CO) (no PMe resonance appeared).

In an approach complementary to that reported above, 0.02 mmol of **2b** or **2c** was mixed with 10 μL (0.09 mmol) of 1,3,5-hexatriene or 30 μL (0.3 mmol) of isoprene in the dark. The reaction mixtures changed color to yellow-brown, but while 1,3,5-hexatriene reacted instantaneously, the reaction with isoprene took ~0.5 h to be completed, in accord with the reported difference in reactivity of these conjugated systems toward $CpM(CO)_3H$ (M = Cr, Mo, W).[13] The products of these reactions, *i.e.* **6a** and **6b**, were identical with those obtained via the above hydride hydrogen atom abstraction by trityl radicals, as shown by IR and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy.

Reactions of 6a with Alkyl Halides. Freshly prepared toluene (3 mL) solutions of **6a** (13 mg, 0.02 mmol), prepared as described above, were treated in the dark with 10-fold molar excesses (~10 μL) of the following alkyl halides: CCl_4, $CHBr_3$, $BrCH_2CN$, ICH_2CO_2Et, allyl iodide, benzyl bromide, $BrCH_2CO_2Me$, ethyl iodide, isopropyl iodide, *tert*-butyl iodide. The reaction mixtures changed color to red in a few seconds with CCl_4, $CHBr_3$, $BrCH_2CN$, ICH_2CO_2Et, and allyl iodide, and in these cases complete consumption of **6a** was established by IR spectroscopy. The reaction products were solely the corresponding dihalides **3b**, **4**, and **5** for allyl iodide, $CHBr_3$, and CCl_4, respectively, all being identified on the basis of comparisons with IR data of the independently characterized dihalides. In the reaction of **6a** with $BrCH_2CN$, dibromide **4** was the major product, although the presence of another significant product was also apparent from the IR spectrum (ν_{CO} 1943 and 1872 cm^{-1}). The $^{31}P\{^1H\}$ NMR spectrum (toluene-d_8) of a similar reaction mixture exhibited, in addition to strong resonances of *cis,cis*-**4** at δ 35.16 and 35.25, several weaker resonances at δ ~48.1−48.6 and at δ 34.45, 34.95, and 35.15. A ^1H NMR spectrum of this solution exhibited strong resonances of *cis,cis*-**4**, the major product, in addition to many other weak, broad, overlapping resonances. Similar results were obtained with ICH_2CO_2Et; in this case the IR spectrum exhibited strong carbonyl bands of **3b** and absorptions of a minor product at 1938 and 1863 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum (toluene-d_8) exhibited, in addition to resonances of **3b**, weaker resonances at δ ~50.8−51.0 and at δ 30.8, 31.3. Benzyl bromide, $BrCH_2CO_2Me$, and *tert*-butyl iodide reacted with **6a** in ~4 h, but the reaction mixtures decomposed during this time and only the formation of *cis,cis*-**3b**, from *t*-BuI, could be verified by IR and ^1H and $^{31}P\{^1H\}$ NMR. No reaction was observed with ethyl and isopropyl iodide over ~4 h.

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(13) Miyake, A.; Kondo, H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 880.

***cis*-$(PMe_2Ph)(CO)_2ICr(\mu\text{-}Fv)$[*trans*-$Cr(CO)_2(PMe_2Ph)_2$]I (7).** To a stirred solution of 0.20 g (0.31 mmol) of $FvCr_2(CO)_6I_2$ in 20 mL of THF was quickly added 0.44 mL (3.1 mmol) of PMe_2Ph, resulting in rapid gas evolution. The reaction mixture was stirred for ~1 h at room temperature in the dark, resulting in formation of a crystalline precipitate. Precipitation was completed by adding 20 mL of hexane to the reaction mixture, the supernatant liquid was decanted and the remaining solid was washed with 5 × 10 mL of hexane and dried under reduced pressure. Yield: 0.23 g (0.23 mmol, 73%). Compound **7** is a purple-brown, crystalline powder which is insoluble in acetone or acetonitrile but of limited solubility in THF and DMSO, giving cherry red solutions. Anal. Calcd for $C_{38}H_{41}Cr_2I_2O_4P_3$: C, 45.08; H, 4.08. Found: C, 44.66; H, 4.28. FAB(+)-MS: m/z (%) $[M]^+ = 885$ (3), $[M - 2CO]^+ = 829$ (9), $[M - I]^+ = 758$ (4), $[M - PMe_2Ph - 2CO]^+ = 691$ (43), $[M - PMe_2Ph - 4CO]^+ = 635$ (44), $[M - I - PMe_2Ph - 2CO]^+ = 564$ (7), $[M - 2PMe_2Ph - 4CO]^+ = 497$ (100), $[M - 3PMe_2Ph - 4CO]^+ = 359$ (81).

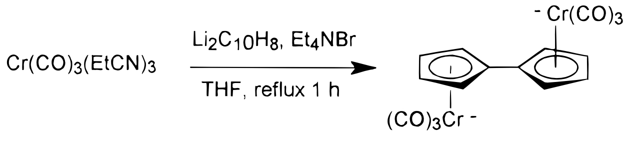
Intermediates in the Reaction of $FvCr_2(CO)_6I_2$ with PMe_2Ph. A 0.03 g (0.05 mmol) amount of $FvCr_2(CO)_6I_2$ was dissolved in 5 mL of THF, and 8 μL (0.05 mmol) of PMe_2Ph was added dropwise at room temperature. An IR spectrum of the reaction mixture taken at this point exhibited strong, broad carbonyl bands at 2033, 1969 (sh), 1956, and 1882 cm^{-1}. After addition of an extra 20 μL (0.10 mmol) of PMe_2Ph, only those at 1956 and 1878 cm^{-1} remained (the latter was slightly shifted from 1882 cm^{-1}). Solvent was evaporated under reduced pressure, and the remaining solid was redissolved in acetone-d_6 for NMR investigations; **7** was identified as the only product. ^1H NMR (acetone-d_6): δ 2.18 (d, $J_{PH} = 8$ Hz, 3H, PMe), 2.20 (d, $J_{PH} = 9$ Hz, 12H, PMe), 2.21 (d, $J_{PH} = 8$ Hz, 3H, PMe), 4.73, 4.81, 4.85, 4.93, 5.07, 5.12 (m, 1H, all Fv), 5.43 (m, 2H, Fv), 7.43 (m, 3H, *m,p*-Ph), 7.56 (m, 6H, *m,p*-Ph), 7.71 (m, 2H, *o*-Ph), 7.80 (m, 4H, *o*-Ph).

In a separate experiment, 10 mg of $FvCr_2(CO)_6I_2$ was mixed with 0.6 mL of acetone-d_6 in an NMR tube, resulting in only partial dissolution of the solid. Into this mixture was injected 1 μL of PMe_2Ph, and formation of $[(CO)_3ICr](\mu\text{-}Fv)[Cr(CO)_3PMe_2Ph]I$ was established by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. This compound readily transformed into a more stable one in ~30 min, and no attempt was made to isolate it. It could be regenerated from the unreacted starting material by addition of 1 μL of PMe_2Ph every ~30 min. During the consumption of $[(CO)_3ICr](\mu\text{-}Fv)[Cr(CO)_3PMe_2Ph]I$, a steady increase in the concentration of *cis*-$[PMe_2Ph(CO)_2ICr](\mu\text{-}Fv)[Cr(CO)_3PMe_2Ph]I$ was observed. This was characterized again by ^1H and $^{31}P\{^1H\}$ spectroscopy. When this sample was kept at room temperature in the dark for ~2 days (containing unreacted $FvCr_2(CO)_6I_2$), formation of a ca. 1:1 mixture of *cis*-$FvCr_2(CO)_5(PMe_2Ph)I_2$ and *cis,cis*-$FvCr_2(CO)_4(PMe_2Ph)_2I_2$ could be established. ^1H NMR for *cis*-$FvCr_2(CO)_5(PMe_2Ph)I_2$ (acetone-d_6): δ 2.13 (d, $J_{PH} = 9$ Hz, 3H, PMe), 2.24 (d, $J_{PH} = 9$ Hz, 3H, PMe), 4.92, 5.18, 5.27, 5.44, 5.48, 5.67 (m, 1H, all Fv), 5.78 (m, 2H, Fv). ^1H NMR for *cis,cis*-$FvCr_2(CO)_4(PMe_2Ph)_2I_2$ (acetone-d_6): δ 2.11 (d, $J_{PH} = 9$ Hz, 6H, PMe), 2.21 (d, $J_{PH} = 9$ Hz, 6H, PMe), 4.81, 4.91, 4.95, 5.03, 5.17, 5.23, 5.52, 5.67 (m, 1H, all Fv), 7.42 (m, 6H, *m, p*-Ph), 7.74 (m, 4H, *o*-Ph). Attempts, however, to prepare [*cis*-$PMe_2Ph(CO)_2ICr](\mu\text{-}Fv)[Cr(CO)_3PMe_2Ph]I$ in pure form failed in THF, as mixtures with *cis,cis*-$FvCr_2(CO)_4(PMe_2Ph)_2I_2$ and $FvCr_2(CO)_6I_2$ were obtained.

Results and Discussion

Synthesis, Characterization, and Reactions of $(Et_4N)_2[FvCr_2(CO)_6]$ (1), $FvCr_2(CO)_6H_2$ (2a), and $FvCr_2(CO)_6I_2$ (3a). These compounds were synthesized in order to secure easily available starting materials for preparation of the phosphine-substituted complexes $FvCr_2(CO)_4L_2X_2$ (X = H, I). It was anticipated that the latter would in turn serve as precursors for the syntheses of the compounds $FvCr_2(CO)_4L_2$ via hydride hydrogen atom abstraction from $FvCr_2(CO)_4L_2H_2$ (eq 1) and/or reduction of $FvCr_2(CO)_4L_2I_2$, as demonstrated previously for molybdenum-containing analogues.[1a,b] Indeed, substitution of the cyclopentadienyl analogues $CpCr(CO)_3X$ (X = H, I) with phosphines as bulky as PPh_3 has been reported[6a,14] and similar behavior of the fulvalene complexes was anticipated.

The anionic complex $(Et_4N)_2[FvCr_2(CO)_6]$ (**1**) was synthesized from $Cr(CO)_3(EtCN)_3$, $Li_2C_{10}H_8$, and Et_4NBr in a "one pot" reaction (eq 3). This procedure is similar to that developed by us to obtain $(Et_4N)_2[FvMo_2(CO)_6]$[1a] and is based on the method of Smart and Curtis for the *in situ* synthesis of $Li_2[FvMo_2(CO)_6]$.[15] Compound **1** was obtained in large quantities and in good yield; although air-sensitive, it can be stored for long periods under nitrogen. It was fully characterized in solution by IR and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, and all data are consistent with the formulation. Thus, the IR spectrum exhibits carbonyl absorbances at 1890, 1800, and 1717 cm^{-1}, similar to those of the Cp analogue (1877, 1765, 1735 cm^{-1} (KBr)),[16] while the ^1H NMR spectrum exhibits, in addition to Et_4N^+ resonances, two fulvalene multiplets at δ 4.13 and 4.61. The $^{13}C\{^1H\}$ NMR spectrum exhibits three fulvalene resonances (δ 80.0, 81.7, 100.9) and a single resonance in the CO region at δ 247.4, identical with that of $Et_4N[CpCr(CO)_3]$.[16] Finally, the known $FvCr_2(CO)_6$[2a,10,11] was formed as the oxidation product when solutions of **1** were exposed briefly to air, confirming the nature of **1**.



(3)

As shown in eq 4, protonation of **1** with glacial acetic acid readily afforded the unstable dihydride $FvCr_2(CO)_6H_2$ (**2a**), which was generated *in situ* for instant use and was characterized by IR and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The IR spectrum exhibited CO absorptions at 2014.5, 1943 and 1940 cm^{-1}, at considerably higher frequencies than for **1** and very similar to those of $CpCr(CO)_3H$ (2018, 1946, 1936 cm^{-1}),[6a] while the ^1H NMR spectrum exhibited two fulvalene (δ 4.08, 4.34) multiplets and a CrH (δ −5.46) resonance. The $^{13}C\{^1H\}$ NMR spectrum exhibited three fulvalene resonances (δ 83.7, 85.9, 99.8) and a CO resonance (δ 234.7); the CO chemical shift is very similar to that of $CpCr(CO)_3H$ (δ 233.5, 242.0 at −80 °C).[17] Furthermore, when **2a** was treated with an excess of isoprene at room temperature, rapid formation of $FvCr_2(CO)_6$, characteristic of the hydridic nature of **2a**, was formed. Similar reactions of $CpCr(CO)_3H$ with conjugated dienes, leading solely to $[CpCr(CO)_3]_2$, have been reported.[3,6a,13]

$$\underset{\text{anion of }\mathbf{1}}{[FvCr_2(CO)_6]^{2-}} + 2H^+ \rightarrow \underset{\mathbf{2a}}{FvCr_2(CO)_6H_2} \qquad (4)$$

Phosphine substitution reactions of **2a** were attempted with PPh_3, PPh_2Me, PMe_2Ph, and PMe_3 with,

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[14] Hackett, P.; O'Neill, P. S.; Manning, A. R. *J. Chem. Soc., Dalton Trans.* **1974**, 1625.

[15] Smart, J. C.; Curtis, C. J. *Inorg. Chem.* **1977**, *16*, 1788.

[16] Behrens, U.; Edelmann, F. *J. Organomet. Chem.* **1984**, *263*, 179.

[17] Alt, H. G.; Engelhardt, H. E.; Kläui, W.; Müller, A. *J. Organomet. Chem.* **1987**, *331*, 317.

respectively, decreasing cone angles and, consequently, decreasing steric requirements.[18] Unfortunately, decomposition to $FvCr_2(CO)_6$ rather than substitution took place with PPh_3 and PPh_2Me in refluxing hexane. However, the smaller phosphines PMe_2Ph and PMe_3 readily reacted with **2a** at room temperature, affording the symmetrically substituted compounds $FvCr_2(CO)_4L_2H_2$ (L = PMe_2Ph (**2b**), PMe_3 (**2c**)) (eq 5), which were

$$\underset{\mathbf{2a}}{FvCr_2(CO)_6H_2} + 2L \rightarrow \underset{\mathbf{2b}\ (L = PMe_2Ph),\ \mathbf{2c}\ (L = PMe_3)}{FvCr_2(CO)_4L_2H_2} + 2CO \quad (5)$$

isolated and characterized (see below). These results show that the chromium compound **2a** exhibits reactivity similar to that of the tungsten analogue $FvW_2(CO)_6H_2$[19] but lower than that of the molybdenum analogue $FvMo_2(CO)_6H_2$.[1a]

Hydrogen−halogen exchange reactions of **2a** with CCl_4, $CHBr_3$, and ICH_2CO_2Et were subsequently attempted but, unlike the case for $FvMo_2(CO)_6H_2$[1a] and $FvW_2(CO)_6H_2$,[19] no reaction occurred with CCl_4 and $CHBr_3$ at room temperature; only slow (1 day) degradation of **2a** to $FvCr_2(CO)_6$ was observed. However, formation of $FvCr_2(CO)_6I_2$ (**3a**) from ICH_2CO_2Et readily occurred (eq 6), and the dihalide was isolated and fully

$$\underset{\mathbf{2a}}{FvCr_2(CO)_6H_2} + 2ICH_2CO_2Et \rightarrow \underset{\mathbf{3a}}{FvCr_2(CO)_6I_2} + 2MeCO_2Et \quad (6)$$

characterized by IR and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and by elemental analyses. The IR spectrum exhibited CO absorptions at 2026, 1972, and 1951 cm^{-1} as anticipated at considerably higher frequencies than for **2a**, while the ^1H NMR spectrum exhibited two fulvalene (δ 5.54, 5.90) multiplets. The $^{13}C\{^1H\}$ NMR spectrum exhibited three fulvalene resonances (δ 91.2, 92.1, 103.2) and two CO resonances at δ 235.9 (*cis* to I) and 247.5 (*trans* to I) in a 2:1 ratio, assigned on the basis of precedents established previously for $FvMo_2(CO)_6X_2$[1a] and $CpMo(CO)_3X$[20] (X = Cl, Br, I). The presence of the byproduct, ethyl acetate, was confirmed by ^1H NMR spectroscopy.

Compound **3a** was also produced in the reaction of $FvCr_2(CO)_6$ with ICH_2CO_2Et. Formation of **3a** in this case probably results from iodine atom abstraction from ICH_2CO_2Et by chromium-centered radicals generated either by heat or by fluorescent lighting and provides additional indirect evidence for the existence of the biradical isomer of $FvCr_2(CO)_6$.[2b]

A reaction of **3a** with PPh_3 was attempted as a possible route to substituted (fulvalene)chromium complexes containing bulky phosphines. However, when a toluene solution of **3a** containing an excess of PPh_3 was heated to 110 °C for 10 min, **3a** completely decomposed to $FvCr_2(CO)_6$ (IR, NMR); no substitution was observed. Note that similar but only partial decomposition of $FvMo_2(CO)_6X_2$ (X = Cl, Br, I) was also observed under identical conditions;[1a] the byproducts of this reaction were not investigated further.

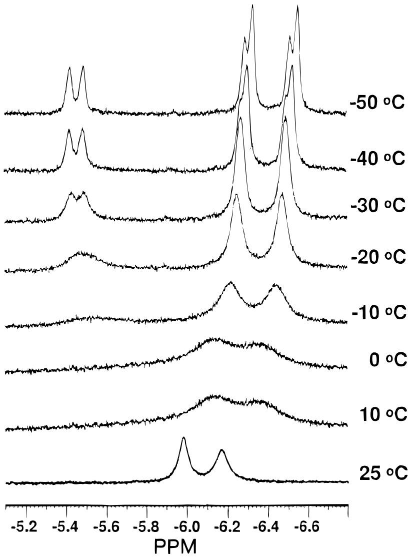

Figure 1. Stacked variable-temperature ^1H NMR spectra of compound **2b** in the hydride region in toluene-d_8.

Characterization of $FvCr_2(CO)_4L_2H_2$ (L = PMe_2Ph (2b), PMe_3 (2c)). These compounds were isolated in good yields by direct substitution of **2a** with the corresponding phosphine. They are fairly stable as solids and were characterized by high-resolution MS, IR, and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR techniques, as well as by elemental analysis for **2b**. While the room-temperature ^1H NMR spectra of **2b** and **2c** were much as expected, with doublets in both the PMe and hydride regions and a pair of virtual quartets in the fulvalene region, no CO or PMe carbon resonances could be observed in the $^{13}C\{^1H\}$ NMR spectra, although resonances of the three different fulvalene carbons in both **2b** and **2c** and all the Ph carbons in **2b** were present. Similar observations have been made with $FvMo_2(CO)_4(PPh_3)_2H_2$, which was shown by variable-temperature ^1H and $^{31}P\{^1H\}$ NMR spectroscopy to be undergoing rapid exchange between *cis* and *trans* isomers.[1a] A brief variable-temperature NMR study of the complex $CpCr(CO)_2(PMe_3)H$ has also been reported.[17]

We therefore carried out variable-temperature (+25 to −60 °C) ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR investigations of **2b** and **2c** in order to study possible isomerization processes and in so doing found that the $FvCr(CO)_2LH$ moieties exist in *cis* and *trans* isomeric forms. The results of the variable-temperature ^1H NMR experiment with **2b** are illustrated in the stacked spectra in Figure 1, which demonstrate the dynamic behavior of this compound. As can be seen, the somewhat asymmetric hydride doublet resonances broaden significantly below room temperature and eventually decoalesce into at least three doublets.

Although the ^1H NMR spectra of **2b** and **2c** were similar in the Cr−H region at −50 °C, we refer here to the better resolved spectrum of **2c** (Figure 2) to discuss the most plausible assignments (see ref 1a or 19 for schemes showing possible isomers). On the basis of characteristic values of the P−H coupling constants for isomers of $CpCr(CO)_2(PMe_3)H$[17] and $FvMo_2(CO)_4L_2H_2$ (L = PPh_3, PMe_3),[1a,19] the two equal upfield (J_{PH} = 92 Hz) doublets probably belong to *cis,cis* isomers (*meso* and *dl*) while the weak downfield doublet (J_{PH} = 28 Hz) may represent the *trans* half of the *cis,trans* isomer. As

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[18] Dias, P. B.; Minas de Piedade, M. E.; Martinho Simões, J. A. *Coord. Chem. Rev.* **1994**, *135/136*, 737.

[19] Tilset, M.; Vollhardt, K. P. C.; Boese, R. *Organometallics* **1994**, *13*, 3146.

[20] Todd, L. J.; Wilkinson, J. R.; Hickey, J. P.; Beach, D. L.; Barnett, K. W. *J. Organomet. Chem.* **1978**, *154*, 151.

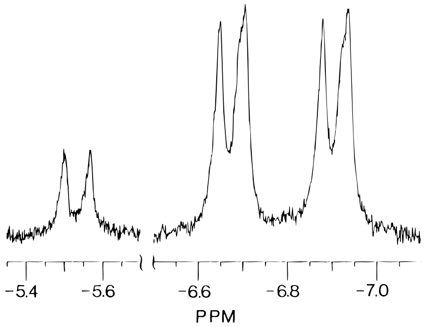

Figure 2. Cr−H proton resonances of compound **2c** at −50 °C in toluene-d_8.

the shoulders evidently indicate, resonances attributable by default to a *trans*,*trans* and *cis* half of the *cis*,*trans* isomer remain hidden underneath the much stronger peaks. Similar assignments can be made for **2b**. Integrations of the resonances were consistent with a 77:23 *cis*:*trans* ratio for **2b** and an 85:15 ratio for **2c**; these differ considerably (in favor of the *cis* form) from those of $FvM_2(CO)_4L_2H_2$ (M = Mo, W; L = PMe_3, PMe_2Ph)[19] and $CpM(CO)_2LH$ (M = Cr, Mo, W; L = PMe_3, PMe_2Ph),[17,21] which typically appear in *cis*:*trans* ratios close to 1. It is also interesting to note that there are separate hydride resonances for the *meso* and *dl* forms of the *cis*,*cis* isomers of **2b** and **2c**.

Consistent with these interpretations, the single $^{31}P\{^1H\}$ resonances observed for **2b** and **2c** at room temperature decoalesced at lower temperatures to two distinct, equal *cis*,*cis* resonances, at δ 61.2 and 61.3 (−50 °C) for **2b** and at δ 48.5 and 48.7 (−30 °C) for **2c**, although the weaker resonances of the minor isomers could not be distinguished. Interestingly, the upfield resonance of **2c** further split into two closely spaced singlets (δ 48.80 and 48.84) upon cooling to −50 °C, probably attributable to the *meso*- and *dl*-*cis*,*cis* isomers. For all previously reported examples of phosphine-substituted hydrido fulvalene complexes $FvM_2(CO)_4L_2H_2$ (M = Mo, L = PMe_3, PPh_3; M = W, L = PMe_3, PMe_2Ph), low-temperature studies revealed the presence of only one doublet in the ^1H and one singlet in the $^{31}P\{^1H\}$ NMR spectra, assignable to both the *meso*- and *dl*-*cis*,*cis* isomers.[1a,19]

The $^{13}C\{^1H\}$ NMR spectrum of **2b** recorded at −60 °C was also consistent with the low-temperature ^1H and $^{31}P\{^1H\}$ NMR observations. The resonances of the major *cis*,*cis* (*meso* and *dl*) isomers were dominant and exhibited CO and PMe resonances which were absent in the room-temperature spectra, confirming the broadening effects of dynamic behavior. Thus, resonances attributable to all types of carbons present in **2b** were clearly visible, including two CO doublets at δ 243.7 (J_{PC} = 6.5 Hz) and 251.4 (J_{PC} = 42 Hz), which probably indicate ligands *cis* and *trans* to the hydride ligand, respectively, on the basis of the P−C coupling constants.[20] There were also observed two doublets at δ 21.8 and 22.5, which may be assigned to the nonequivalent PMe carbon atoms. It is not evident at this point, however, whether the two PMe doublets are to be assigned to diastereotopic carbons of the same ligand bonded to a chiral *cis* isomer, as reported for the proton spectrum of $CpMo(CO)_2(PMe_2Ph)I$,[21c] or to the ligands of different *meso*- and *dl*-*cis*,*cis* isomers.

Hydride Hydrogen Atom Abstraction from 2b and 2c by Trityl Radicals. Characterization of $FvCr_2(CO)_4L_2$ (L = PMe_2Ph (6a), PMe_3 (6b)). Compounds **2b** and **2c** were both treated with 2 equiv of the trityl radical at room temperature, resulting in characteristic color changes from yellow to yellow-brown and complete consumption of the starting materials along with formation of triphenylmethane (^1H NMR) and a single organometallic product, *e.g.* **6a** and **6b**, respectively (eq 7). The products were thoroughly characterized in solution by spectroscopic means but were too unstable to isolate pure. However, the analogous reactions of $FvMo_2(CO)_4L_2H_2$ (L = CO, PMe_3, PPh_3, PXy_3) have been shown to afford the molybdenum−molybdenum-bonded compounds *trans*-$FvMo_2(CO)_4L_2$ (containing both phosphines *trans* to the Mo-Mo bond) as the sole organometallic products,[1b] and similar results for the reactions of **2b** and **2c** would be anticipated. Indeed, the IR spectra of the reaction mixtures exhibited patterns of carbonyl absorbances very similar to those of *trans*-$FvMo_2(CO)_4L_2$, suggesting *trans* structures for **6a** and **6b** and, consequently, a metal−metal bond; medium and very strong bands were observed at 1925 and 1851 cm^{-1}, respectively, for **6a** and at 1923 and 1849 cm^{-1} for **6b**. While the frequencies of these absorbances are almost identical with those of **2b** and **2c**, respectively, the carbonyl bands of the two pairs of compounds **2b** and **2c** versus **6a** and **6b** exhibit significantly different relative intensities.

$$\underset{\mathbf{2b},\ \mathbf{2c}}{FvCr_2(CO)_4L_2H_2} + 2Ph_3C^{\bullet} \rightarrow \underset{\mathbf{6a}\ (L = PMe_2Ph),\ \mathbf{6b}\ (L = PMe_3)}{FvCr_2(CO)_4L_2} + 2Ph_3CH \quad (7)$$

The UV−vis spectra of the products were also consistent with structures containing metal−metal bonds, since both exhibited an intense $\sigma \rightarrow \sigma^*$ transition, at 460 and 455 nm, respectively. The ^1H NMR spectra of **6a** and **6b** provided complementary structural information, exhibiting for PMe, Fv, and Ph resonances with appropriate integrals. In support of the identification of the products as *trans*-$FvCr_2(CO)_4L_2$ (L = PMe_2Ph (**6a**), PMe_3 (**6b**)), they were also prepared via alternative routes, *i.e.* by reacting **2b** and **2c** with 1,3,5-hexatriene and isoprene. We have demonstrated previously that **2a** readily hydrogenates isoprene to form the well-known[2a,10,11] $FvCr_2(CO)_6$, and analogous reactions of the hydrides $CpM(CO)_3H$ (M = Cr, Mo, W) with these conjugated olefins are also known to give the corresponding metal−metal-bonded dimers $[CpM(CO)_3]_2$ via metal-centered radicals.[3,6a,13]

On the other hand, the room-temperature ^1H NMR spectra exhibited anomalous behavior not completely consistent with these formulations of compounds **6a** and **6b**. Thus, while the ^1H NMR spectrum of **6a** exhibits two fulvalene (δ 3.69, 3.92) and a PMe (δ 1.68) resonance, all are broadened and the PMe proton resonance does not exhibit coupling to phosphorus. The ^1H NMR spectrum of **6b** was rather similar, the PMe_3 resonance being a poorly resolved doublet. The room-temperature $^{13}C\{^1H\}$ NMR spectrum of **6a** exhibited only two tertiary fulvalene resonances (δ 82.6, 88.4) but no resonances for the PMe group or any of the quaternary carbon (CO,

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[21] (a) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852. (b) Kalck, P.; Poilblanc, R. *J. Organomet. Chem.* **1969**, *19*, 115. (c) Faller, J. W.; Anderson, A. S.; Jakubowski, A. *J. Organomet. Chem.* **1971**, *27*, C47.

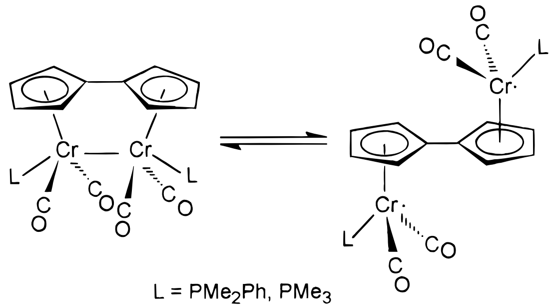
ipso-Ph, C-1 Fv) sites. Similarly, while the room-temperature $^{13}C\{^1H\}$ NMR spectrum of **6b** exhibited a CO doublet and three fulvalene resonances, no PMe resonance was observed. In addition, the $^{31}P\{^1H\}$ NMR spectra of neither **6a** nor **6b** exhibited resonances at room temperature, and it thus seemed likely that compounds **6a** and **6b** exists in rapid equilibrium with one or more other isomers, possibly a paramagnetic diradical species which would be responsible for extensive line broadening in the observed, time-averaged spectra.

In order to support this hypothesis, variable-temperature IR and NMR investigations were carried out with **6a** and **6b**. When solutions of both were cooled below room temperature, resonances in the $^{31}P\{^1H\}$ NMR spectra appeared and, at −40 °C, the spectra exhibited narrow singlet resonances at δ 66.0 and 57.4, respectively (see ref 1c for figure). Similarly, the $^{13}C\{^1H\}$ NMR spectrum of **6a** was recorded at −50 °C and all of the previously missing quaternary and PMe resonances were observed. In particular, a CO doublet at δ 254.8 (J_{PC} = 35 Hz) suggested identical CO ligands being *cis* to PMe_2Ph, supporting a *trans* structure.[1b] The CO carbon resonance of **6b**, evident at room temperature at δ 253.6 (d, J_{PC} = 45 Hz), was also consistent with a *trans* structure.

While the ^1H NMR spectrum of **6a** did not exhibit significant changes below room temperature, both the fulvalene and the methyl resonances gradually shifted downfield and broadened on raising the temperature from 20 to 80 °C; at 80 °C, all of these resonances had broadened sufficiently that they could not be identified. Reversibility of these changes was demonstrated when the sample was cooled back to room temperature, although significant decomposition had taken place. Analogous chemical shift changes and line broadening have also been observed in the variable-temperature ^1H NMR spectra of compounds of the type $[CpCr(CO)_2L]_2$ and have been attributed to extensive dissociation to 17-electron monomers.[5a,b,d]

In a complementary variable-temperature IR spectroscopic study, carried out on **6a** in the temperature range 25−80 °C, the two absorbances of **6a** at 1925 and 1851 cm^{-1} gradually decreased and two new absorbances evolved at 1949 (s) and 1800 (s, br) cm^{-1} as the temperature increased. Only the new bands were present at 80 °C, consistent with the ^1H NMR observation, but the reversibility of the process could not be confirmed because of very extensive decomposition in the IR cell. However, we note that the carbonyl stretching frequencies of the high-temperature species are very similar to those of the persistent metal-centered radical $CpCr(CO)_2PMe_2Ph$ (1925 (s), 1807 (m, br) cm^{-1}),[6a] supporting the identification of this species as the biradical $(Me_2PhP)(CO)_2Cr(\mu\text{-}Fv)Cr(CO)_2(PMe_2Ph)$.

In summary, the most plausible rationale for the temperature dependence of the NMR and IR spectra is that the chromium−chromium-bonded forms of **6a** and **6b** maintain a facile equilibrium with the corresponding radical isomers, as shown in eq 8. The "monomer−dimer" equilibrium shifts toward the diamagnetic, metal−metal-bonded isomer and exchange between the two species slows down considerably at low temperatures; thus, only the "dimers" are observable by IR and NMR spectroscopy below about −40 °C. However, the equilibrium shifts significantly to the right above room temperature, and the paramagnetic, biradical isomers are the predominant species at ~80 °C.



(8)

No attempt was made to carry out solution magnetic susceptibility or EPR experiments. The extent of dissociation is too small for usefully accurate magnetic susceptibilities to be measured by the Evans method,[22] and experience has shown that facile monomer−dimer equilibration in systems such as this invariably leads to sufficient EPR line broadening such that resonances cannot be observed.

The fulvalene ^1H and $^{13}C\{^1H\}$ NMR resonances of the chromium−chromium-bonded form of **6a** and **6b** merit additional comment, since several analogous molybdenum complexes are available for comparison.[1b,23] It has been proposed that the magnetic anisotropy induced by the metal−metal bonds in the dimers *trans*-$FvMo_2(CO)_4L_2$ (L = CO, PMe_3) not only generates a larger chemical shift difference for the fulvalene proton sites (~0.7−0.8 ppm) than is found for many analogous non-metal−metal-bonded complexes (~0.4 ppm) but also results in inversion of the relative positions of the resonances. If so, then the fulvalene ^1H chemical shifts could be diagnostic of the presence of metal−metal bonds in fulvalene complexes in general.[23] We have previously shown, however, that while *trans*-$FvMo_2(CO)_4(PCy_3)_2$ obeys this "rule", the compounds *trans*-$FvMo_2(CO)_4L_2$ (L = PPh_3, PXy_3) do not,[1b] and we now provide further contradictions. The chemical shift difference between the fulvalene proton resonances is only 0.23 ppm in **6a** and is apparently negligible in **6b**, showing that the proposed effects of the metal bond[23] are not applicable to these compounds.

We also previously found that the $^{13}C\{^1H\}$ NMR spectra of the metal−metal-bonded compounds *trans*-$FvMo_2(CO)_4L_2$ (L = PPh_3, PXy_3) exhibit bridgehead (C-1) fulvalene carbon resonances upfield from one of the tertiary fulvalene carbon resonances; this was unusual since, in all other fulvalene complexes, the bridgehead carbons are normally deshielded relative to both the C_α and C_β carbons.[23] Now **6a** provides the third example where the C-1 carbon resonance is also irregularly shielded, although **6b** seems to be normal.

Reactions of 6a with Alkyl Halides. A reaction typical of 17-electron, metal-centered radicals is the abstraction of halogen atoms from organic halides,[4] and the extensive chemistry exhibited by $[CpCr(CO)_3]_2$ with alkyl halides[5e,24] is actually a reflection of the reactivity

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(22) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(23) Meyerhoff, D. J.; Nunlist, R.; Tilset, M.; Vollhardt, K. P. C. *Magn. Reson. Chem.* **1986**, *24*, 709.

(24) (a) Goulin, C. A.; Huber, T. A.; Nelson, J. M.; Macartney, D. H.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1991**, 798. (b) Huber, T. A.; Macartney, D. H.; Baird, M. C. *Organometallics* **1993**, *12*, 4715. (c) Huber, T. A.; Macartney, D. H.; Baird, M. C. *Organometallics* **1995**, *14*, 592.

(25) McLain, S. J. *J. Am. Chem. Soc.* **1988**, *110*, 643.

(26) Kovács, I.; Baird, M. C. *Can. J. Chem.*, in press.

of the monomer $CpCr(CO)_3$, which occurs in the equilibrium mixture as about 10% of the dimer.[5d,25] In general, $CpCr(CO)_3$ abstracts halogen atoms from a number of activated alkyl halides and generates the halide complexes $CpCr(CO)_3X$ (X = Br, I); a second $CpCr(CO)_3$ species then traps the alkyl moieties as the alkyl compounds $CpCr(CO)_3R$ (eq 9).[4,5e,24] In contrast,

$$[CpCr(CO)_3]_2 + RX \rightarrow CpCr(CO)_3X + CpCr(CO)_3R \quad (9)$$

analogous alkyl complexes are not formed in reactions of organic halides with the short-lived, photochemically generated radicals $CpM(CO)_3$ (M = Mo, W) because the low steady-state concentrations of the organic and metal-centered radicals prevent the coupling processes necessary for formation of the products $CpM(CO)_3R$.[5i,j]

To test the chemistry of **6a** and **6b** for radical-like properties, their reactions with alkyl halides have been studied. We find that both **6a** and **6b** react with a variety of activated alkyl halides at room temperature, and the reactions of **6a** have been investigated in detail. IR spectroscopic investigations revealed that **6a** is consumed instantaneously in the dark in the presence of an excess of allyl iodide, $CHBr_3$, or CCl_4 and that the dihalides **3b**, **4**, and **5** (see below for discussion of these compounds) were formed as the sole carbonyl-containing products with allyl iodide, $CHBr_3$, and CCl_4, respectively (eq 10). The reaction of **6a** with *t*-BuI was somewhat

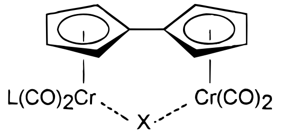
$$\underset{\mathbf{6b}}{FvCr_2(CO)_4(PMe_2Ph)_2} + RX \rightarrow \underset{\mathbf{3b}\ (X = I),\ \mathbf{4}\ (X = Br),\ \mathbf{5}\ (X = Cl)}{FvCr_2(CO)_4(PMe_2Ph)_2X_2} \quad (10)$$

slower (~1 h) and resulted in the formation of **3b**, while those with PhCH(Br)Me, $PhCH_2Br$, and $BrCH_2CO_2Me$ took place at much slower rates (>3 h) such that the expected atom abstraction products decomposed; thus, only degradation of **6a** could be observed. Less active alkyl halides (MeI, EtI, and *i*-PrI) did not exhibit any reactivity at room temperature.

In contrast to the above, the activated alkyl halides $BrCH_2CN$ and ICH_2CO_2Et reacted quickly with **6a** to form the corresponding dihalides **4** (ν_{CO} 1968, 1881 cm^{-1}) and **3b** (ν_{CO} 1958, 1877 cm^{-1}), respectively, in yields of ~70%. Byproducts were also formed with carbonyl stretching bands at 1943, 1872 cm^{-1} and 1938, 1863 cm^{-1}, respectively. These are at somewhat lower frequencies than the dihalides, as would be anticipated for the anticipated halo−alkyl products $FvCr_2(CO)_4(PMe_2Ph)_2(CH_2CN)Br$ and $FvCr_2(CO)_4(PMe_2Ph)_2(CH_2CO_2Et)I$. While chromatographic separations of the highly labile materials failed and the ^1H NMR spectra were too complicated to be interpreted, the $^{31}P\{^1H\}$ NMR spectra exhibited, in addition to resonances of **4** and **3b**, two groups of relatively weak resonances, one with chemical shifts nearly coincident with those of **4** and **3b**, and a second at ~δ 50. By analogy with the hydrido−halides $FvCr_2(CO)_4(PMe_2Ph)_2HX$ and compounds of the type $FvCr_2(CO)_4(PMe_2Ph)_2RR'$,[26] the ^{31}P chemical shift of a PMe_2Ph coordinated to the alkyl "half" of a halo−alkyl Fv compound is expected to be ~δ 58, and thus the $^{31}P\{^1H\}$ NMR data may be consistent with the partial formation of the compounds $FvCr_2(CO)_4(PMe_2Ph)_2(CH_2CN)Br$ and $FvCr_2(CO)_4(PMe_2Ph)_2(CH_2CO_2Et)I$. It is certain, however, that the dialkyl compound $FvCr_2(CO)_4(PMe_2Ph)_2(CH_2CN)_2$ was not formed, as it exhibits quite different IR and $^{31}P\{^1H\}$ NMR spectroscopic properties.[26]

The relative reactivities observed in these experiments, although qualitative, are in good agreement with earlier reports on the relative reactivities of the metal-centered radicals $CpM(CO)_3$ (M = Cr, Mo, W) with alkyl halides[4,5e,i,j,24] and are as anticipated for halogen abstraction reactions for the types of biradical species shown in eq 8. Formation of the halide complexes $FvCr_2(CO)_4(PMe_2Ph)_2X_2$ (X = Cl, Br, I) as the sole or major carbonyl-containing products implies that coupling processes to give Cr−alkyl bonds are not competitive with halogen atom abstractions from excess alkyl halides[5i,j] and is thus consistent with our finding that the equilibrium of eq 8 lies far to the side of the metal−metal-bonded isomer at room temperature. In passing, we note that the types of alkyl halides (XCH_2CN and XCH_2CO_2Et) which appear to give chromium alkyl compounds in the fulvalene systems are also those which give more stable Cp chromium alkyl compounds, presumably because of the effects of electronegative substituents.[5e,24c]

However, the apparent disinclination of the presumed intermediate metal-centered monoradical species $PMe_2Ph(CO)_2Cr(\mu\text{-}Fv)Cr(CO)_2PMe_2PhX$ to couple with organic radicals does seem strange, given the necessarily close proximity of the two metal centers in this compound. Possibly relevant to this anomaly, it has been shown that $CpCr(CO)_3$ and $CpCr(CO)_3I$ take part in an iodine atom exchange process which involves an intermediate of the type $\{CpCr(CO)_3\text{---I---}Cr(CO)_3Cp\}$, formed via interaction of a $CpCr(CO)_3I$ iodine lone pair with the singly occupied orbital of $CpCr(CO)_3$.[5e] If a chelate effect were to apply in the fulvalene system, it is possible that the halogen atom of $PMe_2Ph(CO)_2Cr(\mu\text{-}Fv)Cr(CO)_2(PMe_2Ph)X$ bridges the chromium atoms as in **A**, thereby providing steric hindrance to the "second" chromium or possibly even affecting its electronic properties such that radical-like reactivity is decreased. In fact, a molybdenum analogue of **A** was previously invoked as an intermediate during the hydrogen−halogen atom exchange reactions of alkyl halides with (fulvalene)molybdenum dihydrides $FvMo_2(CO)_4L_2H_2$ (L = CO, PPh_3), where the only significant forward reaction in the presence of an excess of alkyl halide was the abstraction of a second halogen atom to furnish $FvMo_2(CO)_4L_2X_2$.[1a]



A

Hydrogen−Halogen Atom Exchange Reactions of 2b with Activated Alkyl Halides. Independent Characterization of $FvCr_2(CO)_4(PMe_2Ph)_2X_2$ (X = I (3b), Br (4), Cl (5)). To confirm the identities of **3b**, **4**, and **5** as the products of reactions of **6a** with alkyl halides, and possibly to learn more about these new compounds, we developed an alternative route to their syntheses. As demonstrated previously for the PPh_3-substituted molybdenum system, dihalides $FvMo_2(CO)_4$-

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(27) Alt, H. G.; Schwarzle, J. A. *J. Organomet. Chem.* **1978**, *162*, 45.

$(PPh_3)_2X_2$ (X = Cl, Br, I) are readily prepared by the hydrogen-halogen atom exchange reactions of $FvMo_2(CO)_4(PPh_3)_2H_2$ with appropriate alkyl halides.[1a] Analogous reactions of (cyclopentadienyl)- or (fulvalene)-chromium hydrides have not previously been investigated, but the successful preparation of **3a** from **2a** and ICH_2CO_2Et (eq 6) suggested that the dihalides $FvCr_2(CO)_4(PMe_2Ph)_2X_2$ (X = Cl, Br, I) might be obtained similarly. It was also anticipated that phosphine-substituted chromium carbonyl halides could be more stable than the parent carbonyl halide compounds. Thus, while the extremely unstable $CpCr(CO)_3Cl$ may be only briefly detected by IR spectroscopy,[5e] $CpCr(CO)(PMe_3)_2Cl$ has been isolated and fully characterized.[27]

Indeed, **2b** reacted readily with ICH_2CO_2Et, $CHBr_3$, and CCl_4 at room temperature and in the dark, giving the dihalides $FvCr_2(CO)_4(PMe_2Ph)_2X_2$ (X = I (**3b**), Br (**4**), Cl (**5**), respectively) (eq 11). The very labile compounds **4** and **5** were characterized *in situ* by IR and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, as only the iodide **3b** could be isolated analytically pure. In contrast to $FvMo_2(CO)_4(PPh_3)_2X_2$ (X = Cl, Br, I),[1a] **3b** was found to exist as an approximately 1:1 mixture of *meso*- and *dl*-*cis,cis* isomers; thus, eight single-hydrogen fulvalene proton, ten fulvalene carbon, and two (very closely spaced) phosphorus resonances were exhibited in the ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra, as anticipated.[1a] For the same reason, four PMe proton doublets were exhibited in the ^1H NMR spectrum, since the chiral chromium centers further split the two doublets of the *meso* and *dl* forms, rendering the methyl protons of the PMe_2Ph ligand diastereotopic.[21a] Although only three PMe carbon doublets were exhibited in the $^{13}C\{^1H\}$ NMR spectrum, that at δ 19.3 appears to be two completely overlapped doublets, consistent with the ^1H NMR behavior.

$$\underset{\textbf{2b}}{FvCr_2(CO)_4(PMe_2Ph)_2H_2} + RX \longrightarrow FvCr_2(CO)_4(PMe_2Ph)_2HX \xrightarrow{RX} FvCr_2(CO)_4(PMe_2Ph)_2X_2 \qquad (11)$$
$$\textbf{3b}\ (X = I),\ \textbf{4}\ (X = Br),\ \textbf{5}\ (X = Cl)$$

In contrast, compound **4** occurred in solution as the *cis,cis* isomer and compound **5** as a mixture of *cis,cis* and *trans,trans* isomers, the latter being the major product. There was no evidence for formation of the mixed *cis,trans* isomers or, in the case of **4**, of the *trans,trans* isomer. These results seem strange, and while it is possible that weak resonances were obscured, in fact the spectral integrations were as expected. Thus, any minor isomers formed must have been present in very low concentrations.

Interestingly, the preferred isomers of **3b**, **4**, and **5** are the opposite of those of the analogous halo compounds $CpMo(CO)_2(PMe_2Ph)X$, where the chloride and bromide exist predominantly as the *cis* isomer and the iodide exists as a mixture of *cis* and *trans* isomers.[21c] When solutions of the isomeric mixtures of **4** and **5** in CH_2Cl_2 were kept in the dark at room temperature, IR spectroscopic monitoring demonstrated (Figure 3) that thermal decomposition of the *cis* isomers took place considerably faster than that of the *trans* isomers, indicating higher thermal stability of the latter. Compounds *cis,cis*-**3b**, *cis,cis*-**4**, and isomers of **5** were identical with the products of halogen atom abstraction observed in the reaction of **6b** with alkyl halides. The IR spectra of *cis,cis*-**3b**, *cis,cis*-**4**, and *cis,cis*-**5** exhibited carbonyl bands at 1958 and 1877, 1968 and 1881, and 1973 and 1881 cm^{-1}, in the order anticipated.

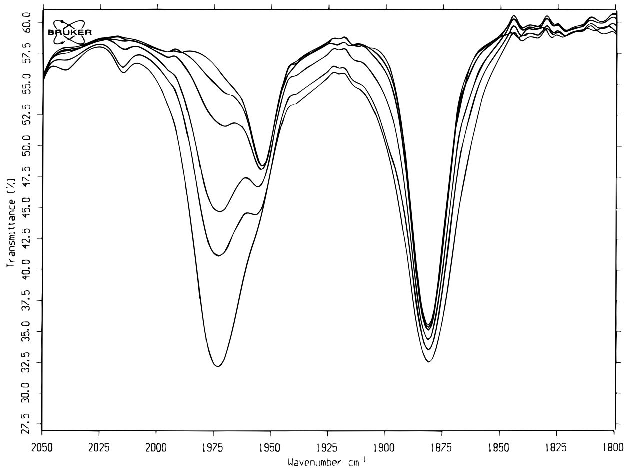


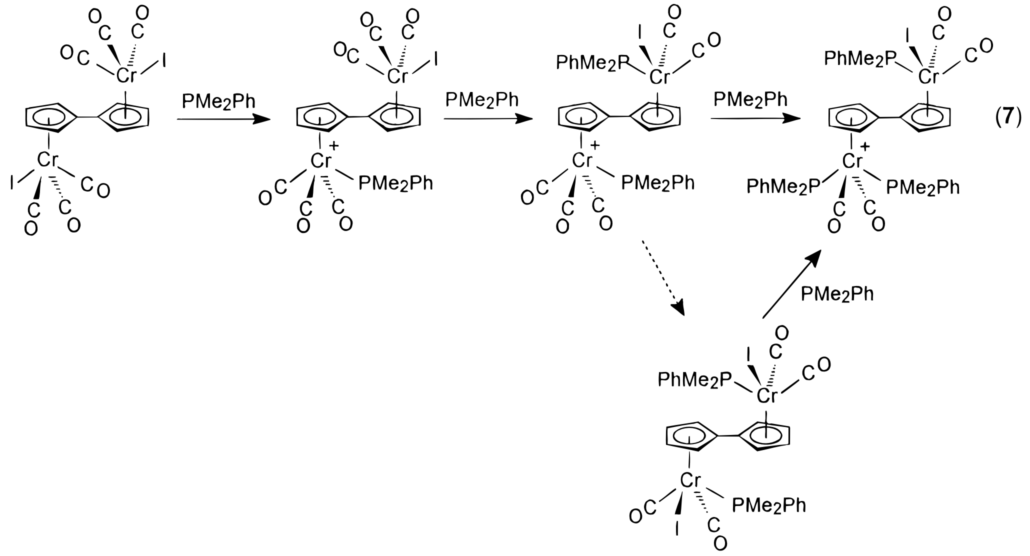
Figure 3. IR spectroscopic monitoring of the spontaneous thermal decomposition of compound **5** in CH_2Cl_2.

Formation of **3b**, **4**, and **5** was established by both ^1H and $^{31}P\{^1H\}$ NMR to proceed stepwise via the intermediate formation of the corresponding hydrido halides *cis*-$FvCr_2(CO)_4(PMe_2Ph)_2HX$ (eq 11), similar again to the molybdenum-containing systems.[1a] It is also interesting to note that only a single intermediate containing a *cis*-halide half was detected in each reaction, suggesting that *cis*−*trans* isomerization of **5**, for example, did not occur before complete halogenation of **2b**. In contrast, $FvMo_2(CO)_4(PPh_3)_2HI$, the intermediate in the reaction of $FvMo_2(CO)_4(PPh_3)_2H_2$ with ICH_2CO_2Et, existed as both *cis*- and *trans*-iodide halves and was ultimately formed in a mixture of *cis,cis*, *cis,trans*, and *trans,trans* diodides.[1a] Another interesting observation was that the radical reaction of **2b** with alkyl iodides and the oxidative cleavage by I_2 both resulted in the sole formation of *cis,cis*-**3b**, although the analogous reactions of $FvMo_2(CO)_4(PPh_3)_2H_2$ afforded different isomers of $FvMo_2(CO)_4(PPh_3)_2I_2$.[1a] Direct substitution of **3a** with PMe_2Ph was also attempted to provide yet another path to **3b**, but this reaction proved to be rather complicated due to formation of various cationic complexes (see below).

Synthesis of *cis*-$PMe_2Ph(CO)_2ICr(\mu\text{-}Fv)[$*trans*-$Cr(CO)_2(PMe_2Ph)_2]I$ (7). When the preparation of **3b** by direct substitution of $FvCr_2(CO)_6I_2$ with excess PMe_2Ph in THF was attempted, a type of reaction which is well documented for $CpCr(CO)_3I$,[14] an IR spectrum of the reaction mixture revealed the rapid formation of a compound displaying two equally strong carbonyl absorbances at 1956 and 1878 cm^{-1}. These frequencies are very similar to those of **3b** (1958, 1877 cm^{-1}) but are of different relative intensities and initially suggested the formation of *trans* isomers of $FvCr_2(CO)_4(PMe_2Ph)_2I_2$. However, a combined ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR investigation unambiguously revealed that the substitution product was in fact the mixed cationic iodide [*cis*-$PMe_2Ph(CO)_2ICr](\mu$-Fv)[*trans*-$Cr(CO)_2(PMe_2Ph)_2]I$ (**7**) (Scheme 1).

Compound **7** was subsequently isolated and characterized by elemental analysis as well. The PMe_2Ph ligands of the cationic chromium center are coordinated in mutually *trans* positions, but the pairs of fulvalene

Scheme 1



proton and carbon atoms are diastereotopic because of the chiral neutral *cis*-Cr(CO)$_2$(PMe$_2$Ph)I moiety.[1a,21a] Although **7** contains neutral and cationic moieties, both chromium centers are formally in the 2+ oxidation state and only a relatively small difference was observed between the bridgehead carbon resonances, at δ 98.4 and 102.8. The ^{31}P{^{1}H} NMR spectrum exhibited two phosphorus resonances at δ 32.9 and 51.1, in a 1:2 ratio of intensities and consistent with the proposed structure.

The formation of **7** was then monitored by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy in acetone-d_6 solution to ascertain the order in which the two metal centers react with the 3 equiv of PMe$_2$Ph, and possibly to gain evidence for intermediates. The phosphine was added in small aliquots to a suspension of (excess) FvCr$_2$(CO)$_6$I$_2$, and spectra were recorded without delay. It was found that a relatively short-lived species was first formed; this exhibited a single phosphorus resonance at δ 41.7 and four fulvalene proton resonances downfield of those of **7**, at δ 5.45, 5.91, 6.12, and 6.44. This compound readily transformed into a more stable species exhibiting two phosphorus resonances of equal intensity at δ 32.7 and 42.0 and eight fulvalene proton resonances at δ 4.96, 5.13, 5.54, 5.81, 5.85, 6.04, 6.26 and 6.38. The phosphorus resonance at δ 32.7, in the region of those of **3b** (δ 33.20 and 33.17), and the presence of eight diastereotopic proton resonances, suggested the formation of a *cis*-Cr(CO)$_2$(PMe$_2$Ph)I moiety. Addition of an excess of PMe$_2$Ph to this mixture resulted in the formation of compound **7**. On the basis of this evidence, the second intermediate was tentatively identified as [*cis*-PMe$_2$Ph(CO)$_2$I]Cr(μ-Fv)[Cr(CO)$_3$PMe$_2$Ph]I and the first, by default, as [(CO)$_3$ICr](μ-Fv)[Cr(CO)$_3$PMe$_2$Ph]I (Scheme 1).

A complementary IR spectroscopic study in THF solution showed that four broad absorbances at 2033, 1969 (sh), 1956, and 1882 cm^{-1} appeared after the addition of only ~1 equiv of PMe$_2$Ph. These were replaced by the two relatively sharp bands of **5** at 1956 and 1878 cm^{-1} when an additional 2 equiv of PMe$_2$Ph was introduced. It seems reasonable that the cationic moieties [Cr(CO)$_3$PMe$_2$Ph]I and [*trans*-Cr(CO)$_2$(PMe$_2$Ph)$_2$]I exhibit carbonyl bands which overlap extensively with those of FvCr$_2$(CO)$_6$I$_2$ and *cis,cis*-FvCr$_2$(CO)$_4$(PMe$_2$Ph)$_2$I$_2$, respectively, and thus that IR spectroscopy cannot be used to unambiguously identify the intermediates observed by NMR spectroscopy.

An example of a cationic fulvalene iodo complex, [FvMo$_2$(CO)$_5$(dmpm)I]I, was obtained recently by reacting the zwitterionic compound FvMo$_2$(CO)$_5$(dmpm) with I$_2$,[19] but the corresponding PMe$_2$Ph-substituted derivative, [(CO)$_3$ICr](μ-Fv)[Cr(CO)$_2$(PMe$_2$Ph)$_2$]I, was not observed here. Furthermore, although this is the first report of formation of cationic chromium complexes from the addition of phosphines to halo complexes of the type Cp′Cr(CO)$_3$X (Cp′ = Cp-like ligand, X = halogen), similar reactions of molybdenum and tungsten Cp complexes are well-documented.[8] However, monodentate phosphines instead substitute one or two CO ligands in CpM(CO)$_3$X (M = Mo, W), and cationic derivatives of the type [CpM(CO)$_2$L$_2$]X (L = CO and/or phosphine) were prepared via alternative ways.[8]

Acknowledgment. We thank NATO for a Science Fellowship to I.K. (administered by the Natural Sciences and Engineering Research Council), the NSERC for a Research Grant to M.C.B., and the Hungarian Science Fund for additional support to I.K. provided by Grant No. OTKA F7419.

OM960051Y