Novel (fulvalene)dichromium alkyl and acyl complexes of the types $FvCr_2(CO)_{6-n}L_nRR'$ and $Et_4N[FvCr_2(CO)_{6-n}L_nR]$ (R, R′ = Me, CH_2CN, COMe; L = CO, PMe_2Ph; n = 0, 1, 2)

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Abstract: The compound $FvCr_2(CO)_6Me_2$ (**1**) is obtained, via the intermediate formation of $Et_4N[FvCr_2(CO)_6Me]$ (**2**), by stepwise addition of 2 equivalents of methyl iodide to $(Et_4N)_2[FvCr_2(CO)_6]$; the analogous cyanomethyl compounds $FvCr_2(CO)_6(CH_2CN)_2$ (**3**) and $Et_4N[FvCr_2(CO)_6(CH_2CN)]$ (**4**) are formed similarly. Compound **1** readily undergoes CO insertion upon treatment with 2 equivalents of PMe_2Ph, giving rise to *trans,trans*-$FvCr_2(CO)_4(PMe_2Ph)_2(COMe)_2$ (**6**), also in two steps via *trans*-$FvCr_2(CO)_5(PMe_2Ph)(Me)(COMe)$ (**8**). The neutral methyl "half" of **2** reacts similarly with PMe_2Ph to form Et_4N[*trans*-$FvCr_2(CO)_5(PMe_2Ph)(COMe)$] (**7**), while the anionic "half" of **2** is alkylated with $ClCH_2CN$ to give $FvCr_2(CO)_6(CH_2CN)Me$ (**5**). Treatment of **5** with PMe_2Ph also results in CO insertion into the Cr—Me bond to give *trans*-$FvCr_2(CO)_5(PMe_2Ph)(CH_2CN)(COMe)$ (**10**). Although **3** is inert to both substitution and insertion reactions with PMe_2Ph, the phosphine-substituted dialkyl (fulvalene)dichromium complex *trans,trans*-$FvCr_2(CO)_4(PMe_2Ph)_2(CH_2CN)_2$ (**9**) is prepared by reaction of $ClCH_2CN$ with $(Et_4N)_2[FvCr_2(CO)_4(PMe_2Ph)_2]$.

Key words: chromium, metal–metal bonds, fulvalene.

Résumé : On a obtenu le composé $FvCr_2(CO)_6Me_2$ (**1**), par le biais de la formation de $Et_4N[FvCr_2(CO)_6Me]$ (**2**), par une addition par étapes de deux équivalents d'iodure de méthyle à du $(Et_4N)_2[FvCr_2(CO)_6]$; les composés cyanométhylés analogues, $FvCr_2(CO)_6(CH_2CN)_2$ (**3**) et $Et_4N[FvCr_2(CO)_6(CH_2)]$ (**4**), se forment de la même manière. Par traitement avec deux équivalents de PMe_2Ph, le composé **1** subit facilement une insertion de CO qui conduit en deux étapes au *trans,trans*-$FvCr_2(CO)_4(PMe_2Ph)_2(COMe)_2$ (**6**) par le biais de l'intermédiaire *trans*-$FvCr_2(CO)_5(PMe_2Ph)(Me)(COMe)$ (**8**). De la même manière, la «moitié» méthylée neutre du composé **2** réagit avec le PMe_2Ph pour conduire à la formation de Et_4N[*trans*-$FvCr_2(CO)_5(PMePh)(COMe)$] (**7**) alors que la «moitié» anionique du composé **2** est alkylée par le $ClCH_2CN$ et conduit au $FvCr_2(CO)_2(CH_2CN)Me$ (**5**). Le traitement du composé **5** à l'aide de PMe_2Ph provoque aussi une insertion de CO dans la liaison Cr—Me et fournit le *trans*-$FvCr_2(CO)_5(PMe_2Ph)(CH_2CN)(COMe)$ (**10**). Même si le composé **3** est inerte aux réactions tant de substitution que d'insertion avec le PMe_2Ph, il est possible de préparer le complexe dialkyl(fulvalène)chrome substitué par une phosphine, *trans,trans*-$FvCr_2(CO)_4(PMe_2Ph)_2(CH_2CN)_2$ (**9**), par réaction du $ClCH_2CN$ avec du $(Et_4N)_2[FvCr_2(CO)_4(PMe_2Ph)_2]$.

Mots clés : chrome, liaisons métal–métal, fulvalène.

[Traduit par la rédaction]

Introduction

In previous papers (1), we have explored the chemistry of fulvalenedichromium and -dimolybdenum complexes of the types $FvM_2(CO)_4L_2$, $FvM_2(CO)_4L_2HX$, $FvM_2(CO)_4L_2H_2$, and $FvM_2(CO)_4L_2X_2$ (M = Cr, Mo; X = Cl, Br, I; L = CO, tertiary phosphines). Following our earlier work on 17-electron, metal-centered radicals (2), the main impetus to this work was a desire, ultimately successful (1c,d), to find and study compounds of the type $FvM_2(CO)_4L_2$ that would undergo spontaneous, thermal metal-metal bond homolysis to give the novel biradical isomers $L(CO)_2M(\mu\text{-}Fv)M(CO)_2L$. In the course of our research, the above-mentioned examples of halo and hydrido classes of compounds were also perforce prepared as starting meterials and (or) products of reactions of the compounds $FvM_2(CO)_4L_2$. We (1a) and others (3) have also demonstrated that protonation of anionic complexes of the type $[FvM_2(CO)_4L_2]^{2-}$ results in the formation of the hydrides $FvM_2(CO)_4L_2H_2$, and we now extend our research on fulvalene complexes to examples of alkyl and acyl (fulvalene)dichromium carbonyl complexes, obtained by treating the anionic species $[FvCr_2(CO)_4L_2]^{2-}$ with various alkyl halides.

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Table 1. Carbonyl stretching frequencies.

Compound	ν_{CO}(cm^{-1})^a
$FvCr_2(CO)_6(CH_3)_2$ (**1**)	2002 (s), 1929 (vs)
$Et_4N[FvCr_2(CO)_6CH_3]$ (**2**)	2000 (s), 1924 (vs), 1902 (s), 1810 (m), 1788 (m), 1727 (m, br)
$FvCr_2(CO)_6(CH_2CN)_2$ (**3**)	2021 (m), 1952 (vs, br)
$Et_4N[FvCr_2(CO)_6CH_2CN]$ (**4**)	2011 (s), 1938 (vs), 1897 (vs), 1795 (vs), 1727 (m, br)
$FvCr_2(CO)_6(CH_2CN)Me$ (**5**)	2021 (m), 2006 (m-s), 1959 (vs), 1931 (s)
trans,trans-$FvCr_2(CO)_4(PMe_2Ph)_2(COMe)_2$ (**6**)	1920 (s), 1840 (vs), 1636 (m)
Et_4N[*trans*-$FvCr_2(CO)_5(PMe_2Ph)COMe$] (**7**)	1920 (s), 1897 (s), 1837.5 (vs), 1808 (m), 1789 (m), 1725 (w, br), 1633 (m)
trans-$FvCr_2(CO)_4(PMe_2Ph)_2(CH_2CN)_2$ (**9**)	1941 (m), 1865 (vs)
trans-$FvCr_2(CO)_5(PMe_2Ph)(CH_2CN)COMe$ (**10**)	2019 (m-s), 1949 (vs), 1922 (m-s, sh), 1844 (s), 1639 (m)
$(Et_4N)_2[FvCr_2(CO)_6]$ ref. (1*d*)	1890 (vs), 1800 (vs), 1717 (s)

^{a}In THF.

Experimental section

General comments

All manipulations were carried out under purified nitrogen using standard Schlenk techniques and a Vacuum Atmospheres glovebox. All solvents were freshly distilled under nitrogen from sodium benzophenone ketyl. Deuterated solvents were purchased from CDN Isotopes and CIL, degassed, and stored in the glovebox. PMe_2Ph, methyl iodide, and chloroacetonitrile were products of Aldrich and were used as received. The compound $(Et_4N)_2[FvCr_2(CO)_6]$ was prepared as previously (1*d*). IR spectra were recorded on a Bruker IFS 25 FT-IR spectrometer using a 0.2-mm NaCl cell. NMR spectra were acquired on a Bruker AM-400 (400.1 MHz ^1H, 100.6 MHz $^{13}C\{^1H\}$, 162.0 MHz $^{31}P\{^1H\}$) NMR spectrometer; IR data are compiled in Table 1. FAB(+)-MS analyses were performed on a Fisons VG Quattro triple quadrupole mass spectrometer using 3-nitrobenzyl alcohol as the matrix. Elemental analyses were carried out by Canadian Microanalytical Services Ltd. (Delta, B.C.).

$FvCr_2(CO)_6Me_2$ (1)

A solution of 0.10 g (0.15 mmol) $(Et_4N)_2[FvCr_2(CO)_6]$ in 5 mL THF was treated with 20 μL (0.32 mmol) of chloroacetonitrile at room temperature. The color changed instantly from yellow to brown, and an IR spectrum indicated that formation of $FvCr_2(CO)_6Me_2$ was complete in ~3 h. Although no other products appeared according to both IR and ^1H NMR studies, evaporation of the solvent resulted in the formation of a yellow-brown oil, which could not be obtained free of THF; some decomposition also occurred, and thus microanalytical characterization of **1** was not successful although all spectroscopic data were consistent with the formulation. ^1H NMR (acetone-d_6), δ: 0.62 (s, 6H, Me), 5.10 ("t," 4H, Fv), 5.37 ("t", 4H, Fv). $^{13}C\{^1H\}$ NMR (acetone-d_6), δ: −5.0 (s, Me), 88.3 (s, Fv), 89.8 (s, Fv), 102.5 (s, C-1 Fv), 238.9 (s, CO *cis* to Me), 249.0 (s, CO *trans* to Me). IR spectroscopic data are shown in Table 1.

$Et_4N[FvCr_2(CO)_6Me]$ (2)

This compound was detected by IR spectroscopy in a reaction carried out as above but with only 0.10 mL of methyl iodide added (Table 1). In an NMR experiment, a solution of 15 mg $(Et_4N)_2[FvCr_2(CO)_6]$ in 0.6 mL acetone-d_6, was treated with methyl iodide dropwise until complete consumption of the starting material had occurred. Since some **1** was always present, no attempt was made to isolate the monomethyl compound, which was unambiguously characterized by IR and NMR spectroscopy. ^1H NMR (acetone-d_6), δ: 0.53 (s, 3H, CrMe), 1.36 (tt, $J_1 = 7$ Hz, $J_2 = 2$ Hz, 12H, CH_2*Me*), 3.42 (q, $J = 7$ Hz, 8H, CH_2N), 4.35, 4.71, 4.80, 4.93 ("t," each 2H, Fv). $^{13}C\{^1H\}$ NMR (acetone-d_6), δ: −2.4 (s, CrMe), 7.7 (s, CH_2*Me*), 52.9 (s, CH_2N), 82.0, 82.3, 86.3, 86.7 (s, all Fv), 90.4 (s, C-1 Fv), 112.9 (s, C-1 Fv), 240.3 (s, CO *cis* to Me), 245.8 (s, CO of anionic moiety), 252.7 (s, CO *trans* to Me).

$FvCr_2(CO)_6(CH_2CN)_2$ (3)

Compound **2** (0.10 g, 0.16 mmol) was dissolved in 5 mL of THF and 20 μL (0.32 mmol) of chloroacetonitrile were injected into the stirred solution at room temperature. The yellow reaction mixture instantly turned deep red and an IR analysis carried out ~1 h later indicated complete consumption of the dianion and formation of a single product, $FvCr_2(CO)_6(CH_2CN)_2$ (Table 1). Evaporation of the solvent resulted in the formation of a red-brown oil. Our attempts to purify this material did not meet with success, but spectroscopic characterization unambiguously established its identity. ^1H NMR (acetone-d_6), δ: 1.62 (s, 4H, CH_2), 5.34 ("t", 4H, Fv), 5.74 ("t", 4H, Fv). $^{13}C\{^1H\}$ NMR (acetone-d_6), δ: −15.4 (s, $CrCH_2$), 89.9 (s, Fv), 93.4 (s, Fv), 102.2 (s, C-1 Fv), 127.4 (s, CN), 238.8 (s, CO *cis* to CH_2CN, 248.2 (s, CO *trans* to CH_2CN).

$Et_4N[FvCr_2(CO)_6(CH_2CN)]$ (4)

A solution of 0.10 g (0.16 mmol) **1** in 5 mL of THF was treated with 10 μL (0.16 mmol) $ClCH_2CN$, added dropwise at room temperature (~10 min). The yellow reaction mixture instantly turned deep red and an IR analysis showed complete consumption of the dianion and formation of $Et_4N[FvCr_2(CO)_6(CH_2CN)]$ (Table 1). Addition of an extra 10 mL of $ClCH_2CN$ transformed this intermediate into **3** within ~2 h without color change. Evaporation of the solvent when only $Et_4N[FvCr_2(CO)_6(CH_2CN)]$ was present resulted in the formation of a red-brown oily residue containing THF, which could not be removed. Attempts to purify this compound led to extensive decomposition to unidentified materials, but it was characterized spectroscopically. ^1H NMR (acetone-d_6), δ: 1.30 (s, 2H, CH_2), 1.36 (tt, $J_1 = 7$ Hz, $J_2 = 2$ Hz, 12H, CH_2*Me*), 3.42 (q, $J = 7$ Hz, 8H, CH_2N), 4.42, 4.82, 5.02, 5.19 ("t," each

2H, Fv). $^{13}C\{^1H\}$ NMR (acetone-d_6), δ: −12.8 (s, $CrCH_2$), 7.7 (s, CH_2*Me*), 52.9 (s, CH_2N), 82.6, 83.0, 86.4 (s, all Fv), 87.9 (s, C-1 Fv), 88.7 (s, Fv), 116.3 (s, C-1 Fv), 128.1 (s, CN), 240.9 (s, CO *cis* to CH_2CN), 245.3 (s, CO of anion), 250.3 (s, CO *trans* to CH_2CN). See Table 1 for IR data.

$FvCr_2(CO)_6(CH_2CN)Me$ (5)

A solution of 0.10 g (0.16 mmol) $(Et_4N)_2[FvCr_2(CO)_6]$ was dissolved in 5 mL of THF and reacted with 10 μL (0.16 mmol) of $ClCH_2CN$, added dropwise at room temperature. The yellow reaction mixture instantly turned deep red and an IR analysis showed complete consumption of the dianion and formation of $Et_4N[FvCr_2(CO)_6(CH_2CN)]$. Addition of 10 μL (0.16 mmol) of methyl iodide transformed this intermediate into compound **5** in ~2 h (IR). Evaporation of the solvent resulted in the formation of a red-brown oil, but attempts to further purify the material were unsuccessful. Nevertheless, **5** was satisfactorily characterized spectroscopically in solution and its identity seems firmly established. ^1H NMR (acetone-d_6): δ: 0.64 (s, 3H, Me), 1.59 (s, 2H, CH_2), 5.11, 5.30, 5.48, 5.64 ("t", each 2H, Fv). $^{13}C\{^1H\}$ NMR (acetone-d_6), δ: −15.8 (s, CH_2), −5.2 (Me), 88.7, 89.1, 90.5, 92.6 (s, all Fv), 100.6 (s, C-1 Fv), 103.9 (s, C-1 Fv), 127.5 (s, CN), 238.6 (s, CO *cis* to Me), 239.2 (s, CO *cis* to CH_2CN), 248.5 (s, CO *trans* to CH_2CN), 248.6 (s, CO *trans* to Me). For IR data see Table 1.

trans,trans-$FvCr_2(CO)_4(PMe_2Ph)_2(COMe)_2$ (6)

A solution of **1**, prepared as above, was evaporated to dryness and the resulting brown material was redissolved in a 2:1 toluene–hexane solvent mixture. Addition of 0.6 mL (4.2 mmol) of PMe_2Ph resulted in precipitation of a yellow solid. A second, smaller crop of precipitate was recovered from the decanted solvent by concentrating under reduced pressure. The combined yellow solids were washed with 5 × 20 mL of hexane and dried. Yield: 0.74 g (1.05 mmol, 86%). The product was recrystallized from THF–hexane at −20°C, but did not give analytically pure samples. However, spectroscopic and mass spectrum data were consistent with the proposed structure. ^1H NMR (acetone-d_6), δ: 1.87 (d, J_{PH} = 9 Hz, 12H, PMe), 2.35 (s, 6H, COMe), 4.26 (m, 4H, Fv), 4.53 (m, 4H, Fv), 7.45 (m, 6H, *m,p*-Ph), 7.69 (m, 4H, *o*-Ph). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ: 18.8 (d, J_{PC} = 30 Hz, PMe), 49.4 (s, CO*Me*), 91.9 (s, Fv), 93.4 (s, Fv), 103.9 (s, C-1 Fv), 129.3 (d, J_{PC} = 9 Hz, *o*-Ph), 130.0 (d, J_{PC} = 8 Hz, *m*-Ph), 130.2 (s, *p*-Ph), 140.8 (d, J_{PC} = 38 Hz, *ipso*-Ph), 250.8 (d, J_{PC} = 45 Hz, CO), 272.4 (d, J_{PC} = 18 Hz, *C*OMe). $^{31}P\{^1H\}$ NMR (acetone-d_6), δ: 58.2. FAB(+)-MS, *m/z*(%): $[M + H]^+$ = 707(0.7), $[M - 3CO - Me]^+$ = 607(1), $[M - 4CO - Me]^+$ = 579(1), $[M - 4CO - 2Me]^+$ = 564(2.5), $[M - PMe_2Ph - 2CO]^+$ = 512(10), $[M - PMe_2Ph - 3CO]^+$ = 484(3), $[M - PMe_2Ph - 4CO]^+$ = 456(8), $[M - PMe_2Ph - 4CO - Me]^+$ = 441(4), $[M - 2PMe_2Ph - 4CO]^+$ = 318(41). IR data are listed in Table 1.

Reaction of freshly generated **3** (0.04 mmol) with 20 μL (0.14 mmol) of PMe_2Ph was attempted in 5 mL THF solution, both thermally and photochemically. In an experiment carried out at room temperature and ambient light over 3 days, the reaction mixture decomposed and a precipitate formed in a green solution; only very weak carbonyl bands were detected in the IR spectrum, at 1944 and 1869 cm^{-1}. Irradiation of a solution of **3** and PMe_2Ph with a 200-W Hanovia lamp led to the same result, but much more quickly (~3 h).

$Et_4N[$*trans*-$FvCr_2(CO)_5(PMe_2Ph)(COMe)]$ (7)

This compound was characterized spectroscopically in situ when an acetone-d_6 solution of $(Et_4N)_2[FvCr_2(CO)_6]$ (15 mg) was "titrated" consecutively with equimolar amounts of methyl iodide and PMe_2Ph at room temperature. ^1H NMR (acetone-d_6), δ: 1.36 (tt, J_1 = 7 Hz, J_2 = 2 Hz, 12H, CH_2*Me*), 1.89 (d, J_{PH} = 9 Hz, 6H, PMe), 2.37 (s, 3H, COMe), 3.42 (q, *J* = 7 Hz, 8H, CH_2N), 4.23 ("t", 2H, Fv), 4.40 (m, 2H, Fv), 4.46 (m, 2H, Fv), 4.54 ("t," 2H, Fv), 7.43 (m, 3H, *m,p*-Ph), 7.74 (m, 2H, *o*-Ph). $^{13}C\{^1H\}$ NMR (acetone-d_6), δ: 18.7 (d, J_{PC} = 30 Hz, PMe), 49.5 (s, CO*Me*), 81.6, 82.1, 90.9, 91.7 (s, all Fv), 92.0 (s, C-1 Fv), 111.7 (s, C-1 Fv), 129.1 (d, J_{PC} = 8 Hz, *o*-Ph), 130.0 (s, *p*-Ph), 130.1 (d, J_{PC} = 8 Hz, *m*-Ph), 141.2 (d, J_{PC} = 37 Hz, *ipso*-Ph), 246.2 (s, CO of anion), 251.3 (d, J_{PC} = 44 Hz, CO of CrCOMe). $^{31}P\{^1H\}$ NMR (acetone-d_6), δ: 59.0. For IR see Table 1.

trans-$FvCr_2(CO)_5(PMe_2Ph)Me(COMe)$ (8)

This compound was observed in NMR scale reactions when PMe_2Ph was added slowly to **1** dissolved in 0.6 mL of acetone-d_6, or when methyl iodide was added to the in situ generated $Et_4N[$*trans*-$FvCr_2(CO)_5(PMe_2Ph)(COMe)]$. Both reactions resulted in various mixtures of this compound and **2**. ^1H NMR (acetone-d_6), δ: 0.50 (s, 3H, CrMe), 1.96 (d, J_{PH} = 9 Hz, 6H, PMe), 2.38 (s, 3H, COMe), 4.58 (m, 2H, Fv), 4.72 (m, 2H, Fv), 4.86 ("t," 2H, Fv), 4.93 ("t", 2H, Fv), 7.46 (m, 3H, *m, p*-Ph), 7.74 (m, 2H, *o*-Ph). $^{13}C\{^1H\}$ NMR (acetone-d_6), δ: −4.8 (s, CrMe), 18.8 (d, J_{PC} = 30 Hz, PMe), 49.4 (s, CO*Me*), 88.3, 88.9, 92.4, 93.6 (s, all Fv), 102.7 (s, C-1 Fv), 104.0 (s, C-1 Fv), 129.35 (d, J_{PC} = 9 Hz, *o*-Ph), 130.1 (d, J_{PC} = 8 Hz, *m*-Ph), 130.3 (s, *p*-Ph), 140.7 (d, J_{PC} = 39 Hz, *ipso*-Ph), 239.3 (s, CO cis to Me), 249.5 (CO *trans* to Me), 250.7 (d, J_{PC} = 44 Hz, CO cis to COMe). $^{31}P\{^1H\}$ NMR (acetone-d_6), δ: 57.9.

trans,trans-$FvCr_2(CO)_4(PMe_2Ph)_2(CH_2CN)_2$ (9)

A solution of 0.30 g (0.34 mmol) $FvCr_2(CO)_4(PMe_2Ph)_2I_2$ (4d) was dissolved in 10 mL of THF and mixed with a large excess of sodium suspension (prepared from sodium dispersion in mineral oil (Aldrich) by washing with 3 × 10 mL of hexane) in 10 mL of THF. The reaction mixture immediately changed color from purple to yellow, but stirring was continued for 1 h. The reaction mixture, containing $Na_2[FvCr_2(CO)_4(PMe_2Ph)_2]$ (IR, ν_{CO}: 1778 and 1680 cm^{-1}) (4d), was filtered through Celite to give a clear, golden-yellow filtrate, which was reacted with 30 μL (0.47 mmol) of chloroacetonitrile. After 3 h, the NaCl precipitate was filtered off, the reaction mixture was concentrated to ~3 mL, and the alkyl complex was precipitated with 10 mL of hexane and collected and dried under reduced pressure. *trans,trans*-**9** was obtained as a poorly soluble, yellow powder in 0.22 g (0.31 mmol), 91 % yield. ^1H NMR (acetone-d_6), δ: 1.23 (d, J_{PH} = 2 Hz, 4H, CH_2), 1.91 (d, J_{PH} = 9 Hz, 12H, PMe), 4.55 (m, 4H, Fv), 4.58 (m, 4H, Fv), 7.50 (m, 6H, *m,p*-Ph), 7.74 (m, 4H, *o*-Ph). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ: −14.9 (d, J_{PC} = 15 Hz, CH_2), 19.2 (d, J_{PC} = 31 Hz, PMe), 88.1, 89.8 (s, both Fv), 100.5 (s, C-1 Fv), 128.5 (d, J_{PC} = 9 Hz, *o*-Ph), 129.3 (s, CN), 129.6 (d, J_{PC} = 7 Hz, *m*-Ph), 129.7 (s, *p*-Ph), 139.1 (d, J_{PC} = 39 Hz, *ipso*-Ph), 251.6 (d, J_{PC} = 46 Hz, CO). $^{31}P\{^1H\}$ NMR (acetone-d_6), δ: 61.2. FAB(+)-MS, m/z(%) $[M + Na]^+$ = 723(1), $[M - 2CO]^+$ = 644(1.5), $[M - 2CO - CH_2CN]^+$ = 604(2), $[M - 4CO - CH_2CN]^+$ = 548(4), $[M - PMe_2Ph - 4CO]^+$ = 450(13.5), [M

$-$ PMe$_2$Ph $-$ 4CO $-$ CH$_2$CN]$^+$ = 410(25), [M $-$ PMe$_2$Ph $-$ 4CO $-$ 2CH$_2$CN]$^+$ = 370(8), [M $-$ 2PMe$_2$Ph $-$ 4CO]$^+$ = 312(31), [M $-$ 2PMe$_2$Ph $-$ 4CO $-$ CH$_2$CN]$^+$ = 272(22.5). IR data are listed in Table 1.

trans-FvCr$_2$(CO)$_5$(PMe$_2$Ph)(CH$_2$CN)(COMe) (10)

A solution of 0.27 g (0.41 mmol) (Et$_4$N)$_2$[FvCr$_2$(CO)$_6$] in 45 mL of THF was reacted with 25 μL (0.41 mmol) of ClCH$_2$CN, added at room temperature. The mixture turned red instantly, and IR spectroscopic monitoring indicated completion of the formation of Et$_4$N[FvCr$_2$(CO)$_6$CH$_2$CN] in ~1 h. At this point, 50 μL (0.80 mmol) of methyl iodide were added and complete formation of **3** was observed after ~1 h. The resulting brown solution was then stirred with 0.15 mL (1.05 mmol) of PMe$_2$Ph for 0.5 h, and an IR spectrum showed that compound **4** was the only carbonyl containing product. The solvent was removed under reduced pressure and 40 mL of a 1:1 THF-hexane mixture was used to extract **4** from the resulting solid. This solution was filtered and evaporated to dryness to give 0.15 g (0.25 mmol, 62%) of a yellow-brown solid. Although attempted recrystallizations did not result in analytically pure product, **4** was thoroughly characterized by spectroscopic means. ^{1}H NMR (acetone-d_6), δ: 1.43 (s, 2H, CH$_2$), 1.98 (d, J_{PH} = 9 Hz, PMe), 2.40 (s, 3H, COMe), 4.70 (m, 2H, Fv), 4.76 (m, 2H, Fv), 5.08 ("t," 2H, Fv), 5.22 ("t", 2H, Fv), 7.47 (m, 3H, *m*,*p*-Ph), 7.76 (m, 2H, *o*-Ph). ^{13}C{^{1}H} NMR (acetone-d_6), δ: $-$15.3 (s, CrCH$_2$), 18.9 (d, J_{PC} = 31 Hz, PMe), 49.4 (s, CO*Me*), 89.2, 91.7, 93.0, 94.0 (s, all Fv), 101.2 (s, C-1 Fv), 105.9 (s, C-1 Fv), 127.6 (s, CN), 129.5 (d, J_{PC} = 9 Hz, *o*-Ph), 130.2 (d, J_{PC} = 7 Hz, *m*-Ph), 130.5 (s, *p*-Ph), 140.7 (d, J_{PC} = 38 Hz, *ipso*-Ph), 239.8 (s, CO cis to CH$_2$CN), 249.2 (s, CO *trans* to CH$_2$CN), 250.6 (d, J_{PC} = 44 Hz, CO of CrCOMe), 271.9 (d, J_{PC} = 18 Hz, *C*OMe). ^{31}P{^{1}H} NMR (acetone-d_6), δ: 57.5. FAB(+)-MS, *m/z*(%): (No [M]$^+$ appeared) [M $-$ CO]$^+$ = 565(2), [M $-$ 2CO]$^+$ = 537(3), [M $-$ 6CO]$^+$ = 425(7.5), [M $-$ 6CO $-$ Me]$^+$ = 410(17), [M $-$ PMe$_2$Ph $-$ 2CO]$^+$ = 399(13), [M $-$ 6CO $-$ Me $-$ CH$_2$CN]$^+$ = 370(27), [M $-$ PMe$_2$Ph $-$ 6CO]$^+$ = 287(15), [M $-$ PMe$_2$Ph $-$ 6CO $-$ Me]$^+$ = 272(27). IR data are listed in Table 1.

Results and discussion

Dianionic fulvalene complexes, [FvM$_2$(CO)$_6$]$^{2-}$ (M = Mo, W), have been shown to undergo nucleophilic reactions with various alkyl halides to give dialkyl derivatives of the types FvM$_2$(CO)$_6$R$_2$ (R = Me, CH$_2$Ph, CH$_2$OMe, etc.) (3*a*,*b*), Not reported to date, however, are analogous reactions of the anionic complex [FvCr$_2$(CO)$_6$]$^{2-}$, which is expected to react with alkyl halides as in eq. [1] to give alkylchromium species. We now report the results of an investigation of such reactions.

$$[1]\quad [\mathrm{FvCr_2(CO)_6}]^{2-} + 2\mathrm{RX} \rightarrow \mathrm{FvCr_2(CO)_6R_2} + 2\mathrm{X}^-$$

To our surprise, addition of BrCH$_2$CN to a THF solution of (Et$_4$N)$_2$[FvCr$_2$(CO)$_6$] did not result in the formation of the anticipated dialkyl product, but resulted instead in oxidation to FvCr$_2$(CO)$_6$ (1*c*, *d*). Similar reactions with XCH$_2$CO$_2$Et (X = Cl, Br, I) were also briefly investigated by IR and ^{1}H NMR spectroscopy, and all resulted in the formation of FvCr$_2$(CO)$_6$. ^{1}H NMR spectra of the reaction mixtures temporarily exhibited very broad fulvalene resonances before those of FvCr$_2$(CO)$_6$ began to emerge, and it would seem that electron-transfer-initiated radical reactions rather than nucleophilic substitutions take place, resulting in metal-metal bond formation. We obtained similar results for the reaction of (Et$_4$N)$_2$[FvMo$_2$(CO)$_6$] with BrCH$_2$CN, and similar reactions have been reported for mononuclear metal carbonyl anions (4).

Hexacarbonyl Alkyl Compounds

Not all alkyl halides oxidize the [FvCr$_2$(CO)$_6$]$^{2-}$ anion, however. Treatment of (Et$_4$N)$_2$[FvCr$_2$(CO)$_6$] with 2 equivalents or more of methyl iodide resulted in the formation of the rather unstable dimethyl compound FvCr$_2$(CO)$_6$Me$_2$ (**1**) (eq. [2], Scheme 1).

$$[2]\quad (\mathrm{Et_4N})_2[\mathrm{FvCr_2(CO)_6}] + 2\mathrm{MeI} \rightarrow \underset{\mathbf{1}}{\mathrm{FvCr_2(CO)_6Me_2}}$$

Compound **1** was thoroughly characterized by spectroscopic methods and the data are fully consistent with the structure shown in Scheme 1. Thus the ^{1}H NMR spectrum exhibited a Cr-Me resonance at δ 0.62 and fulvalene multiplets at δ 5.10 and 5.37, while the ^{13}C{^{1}H} NMR spectrum exhibited a relatively shielded Cr-Me resonance at δ -5.0, fulvalene resonances at δ 88.3, 89.8, and 102.5, and two CO resonances at δ 238.9 (cis to Me) and 249.0 (trans to Me). Assignments of the ^{13}C resonances were made on the basis of data for CpMo(CO)$_3$Me (5), and the results imply that the CO ligands do not interchange on the NMR time scale. While this work was in progress we learned that compound **1** has also been prepared by McGovern and Vollhardt.[3]

When only 1 equivalent of MeI was slowly added to a solution of dianion, the very sensitive, monoanionic intermediate Et$_4$N[FvCr$_2$(CO)$_6$Me] (**2**) could be identified (Scheme 1). All spectroscopic data for this unstable species are consistent with the suggested structure, the ^{1}H NMR spectrum exhibiting a methyl resonance (δ: 0.53) and two sets of fulvalene hydrogens. Similarly the ^{13}C{^{1}H} NMR spectrum exhibited a Cr-Me resonance at δ $-$2.4, two sets of fulvalene resonances, and three CO resonances, two for the neutral and one for the anionic "half."

It is interesting to note that the IR spectrum exhibited one set of carbonyl bands of frequencies comparable with those of **1** (2000 and 1924 cm^{-1}) and a second set of considerably lower frequencies (1902, 1810, 1788 and 1727 cm^{-1}), comparable with those of (Et$_4$N)$_2$[FvCr$_2$(CO)$_6$] (Table 1). Thus the chromium atoms of the two "halves" of **2** appear to be in very different electronic environments. Possibly a result of this dissimilarity is the large difference (22.5 ppm) between the two Fv C-1 carbon resonances, at δ 90.4 and 112.9.

Surprisingly, when (Et$_4$N)$_2$[FvCr$_2$(CO)$_6$] was treated with an excess not of BrCH$_2$CN but of ClCH$_2$CN, complete formation of FvCr$_2$(CO)$_6$(CH$_2$CN)$_2$ (**3**) took place at room temperature (eq. [3]), no FvCr$_2$(CO)$_6$ being formed at all.

$$[3]\quad [\mathrm{FvCr_2(CO)_6}]^{2-} + 2\ \mathrm{ClCH_2CN} \rightarrow \underset{\mathbf{3}}{\mathrm{FvCr_2(CO)_6(CH_2CN)_2}}$$

The product was characterized by IR and NMR spectroscopy, although it could not be isolated analytically pure. However,

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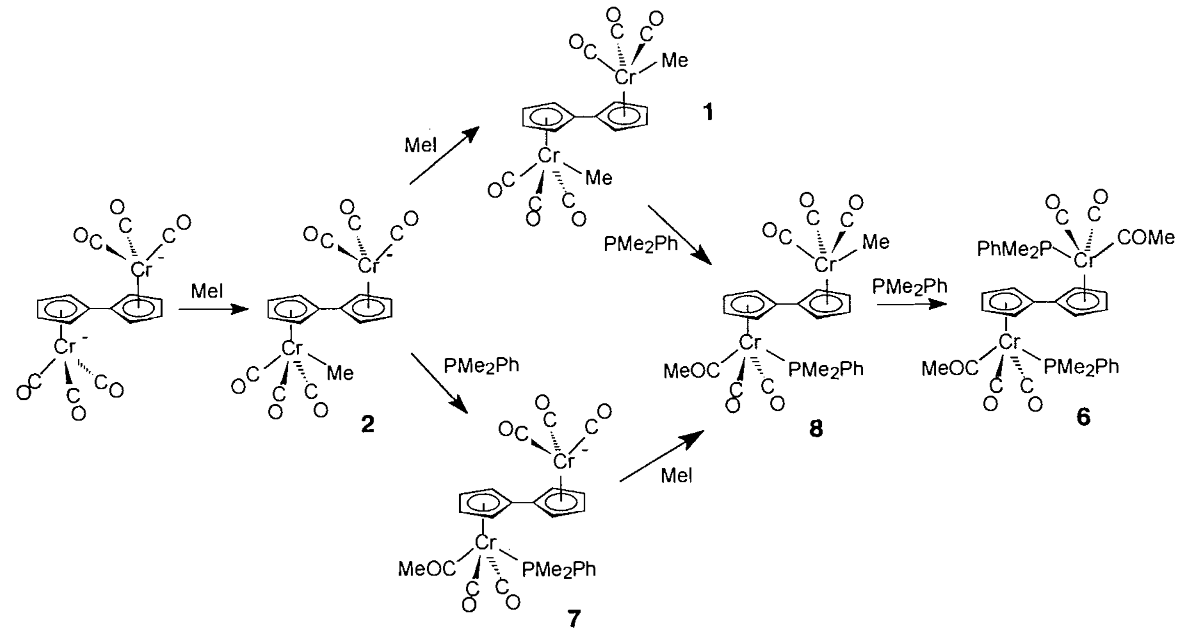
[3] P.A. McGovern and K.P.C. Vollhardt, private communication.

Scheme 1.



the ^1H and $^{13}C\{^1H\}$ NMR spectra exhibit patterns of resonances similar to those of **1**, the $CrCH_2$ proton and carbon resonances appearing at δ 1.62 and −15.4, respectively. Two resonances were observed in the CO region at δ 238.8 (*cis* to CH_2) and 248.2 (*trans* to CH_2) in about 2:1 ratio, suggesting a lack of interchange of these ligands. The carbonyl stretching bands of **3** are observed at higher frequencies than those of **1**, consistent with the greater electron-withdrawing power of the cyanomethyl group. The reasons for the differences in products from reactions of $(Et_4N)_2[FvCr_2(CO)_6]$ with $BrCH_2CN$ and $ClCH_2CN$ are not at all clear; understanding must await a mechanistic study.

Interestingly, when only 1 equivalent of $ClCH_2CN$ was slowly added to a solution of $(Et_4N)_2[FvCr_2(CO)_6]$, sole formation of the anionic alkyl intermediate $Et_4N[FvCr_2(CO)_6(CH_2CN)]$ (**4**) was observed, confirming the intermediacy of this complex in eq.[3]. This anionic alkyl compound was also too labile to be obtained pure, but was characterized spectroscopically. As is the case with **2**, the IR spectrum of **4** suggests the presence of "neutral" (2011 and 1938 cm^{-1}) and "anionic" (1897, 1795, and 1727 cm^{-1}) "halves," and the ^1H and $^{13}C\{^1H\}$ NMR spectra exhibit two sets of resonances. Also, as with **2**, the $^{13}C\{^1H\}$ NMR spectrum of **4** exhibited an unusually large difference (~28 ppm) between the two fulvalene bridgehead carbon resonances, at δ 87.9 and 116.3. Reaction of **4** with a second equivalent of $ClCH_2CN$ to give **3** was, because of decreased nucleophilicity of the monoanion, rather slow (~1 h) relative to the very rapid reaction with the first equivalent.

Successful formation of the anionic alkyl compounds $(Et_4N)[FvCr_2(CO)_6Me]$ (**2**) and $(Et_4N)[FvCr_2(CO)_6(CH_2CN)]$ (**4**) offered opportunities to synthesize mixed dialkyl complexes, and the compound $FvCr_2(CO)_6(CH_2CN)Me$ (**5**) was prepared as outlined in eq. [4], via addition of MeI to $(Et_4N)[FvCr_2(CO)_6(CH_2CN)]$. The product was thoroughly characterized spectroscopically. As can be seen in Table 1, the IR spectrum clearly exhibited two pairs of carbonyl stretching bands, one pair at 2006 and 1931 cm^{-1} attributable to the methyl "half," and another at 2021 and 1959 cm^{-1} that is attributable to the cyanomethyl "half." (Compare with data for **1** and **3**.) Furthermore, the ^1H NMR spectrum exhibited Me and CH_2 resonances at δ 0.64 and 1.59, respectively, and two sets of fulvalene resonances, while the $^{13}C\{^1H\}$ NMR spectrum exhibited Me and CH_2 resonances at δ −5.2 and −15.8, respectively, a CN resonance, and two sets each of fulvalene and CO resonances.

$$[4] \quad \underset{\mathbf{4}}{(Et_4N)[FvCr_2(CO)_6(CH_2CN)]} + MeI \rightarrow \underset{\mathbf{5}}{FvCr_2(CO)_6(CH_2CN)Me}$$

Tertiary phosphine-substituted compounds

In an unsuccessful attempt to synthesize phosphine-substituted analogues of **1**, it was found that **1** readily *added* 2 equivalents of PMe_2Ph at room temperature. The consequence was a sequence of migratory CO insertion reactions into the Cr—Me bonds (eq. [5]), resulting in formation of the diacetyl compound $FvCr_2(CO)_4(PMe_2Ph)_2(COMe)_2$ (**6**) in good yield. Although **6** is also too unstable to be isolated analytically pure, the mass spectrum and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra are all completely consistent with the *trans,trans* structure shown in Scheme 1. Thus the FAB mass spectrum exhibited a protonated molecular ion and several reasonable fragmentation peaks. In addition, the ^1H and $^{13}C\{^1H\}$ NMR spectra each exhibited only single acetyl Me and PMe resonances and single sets of fulvalene resonances, consistent with a symmetrical *trans,trans* structure (see experimental section), while the $^{31}P\{^1H\}$ NMR spectrum exhibited only one singlet. The $^{13}C\{^1H\}$ NMR spectrum exhibited only one doublet for two CO ligands, at δ 250.8 and with a relatively large (J_{PC} 45 Hz) coupling constant suggestive of a *cis*-P-Cr-CO and consequently a *trans*-P-Cr-COMe arrangement (5). The MeCO resonance appeared at δ 272.4 (J_{PC} 18 Hz), quite similar to that of $CpMo(CO)_2(PMe_2Ph)COMe$ (266.8 (12.5)) (5).

$$[5]\quad \underset{\mathbf{1}}{FvCr_2(CO)_6Me_2} + 2PMe_2Ph \rightarrow \underset{\mathbf{6}}{\mathit{trans,trans}\text{-}FvCr_2(CO)_4(PMe_2Ph)_2(COMe)_2}$$

To our knowledge, **6** is the first well-characterized acylchromium complex of the type $CpCr(CO)_2L(COMe)$ (L = phosphorus donor) that has been prepared via a spontaneous, ligand-assisted CO insertion into a Cr–alkyl bond. Two other examples of compounds of the type $CpCr(CO)_2L(COMe)$ were prepared as minor products, either in photochemical substitution reactions of $CpCr(CO)_3Me$ with L (L = PPh_3, $P(OMe)_3$) (6*a*) or in an apparent Arbuzov reaction of $[CpCr(CO)_2\{P(OMe)\ 63\}]$ with $P(OMe)_3$ (6*b*); both exist as mixtures of *cis* and *trans* isomers. Indeed, although photochemical substitution reactions of complexes of the type $CpCr(CO)_3R$ (R = alkyl) with phosphorus donors have attracted a great deal of attention, reactions invariably resulted in the formation of mono- and bis-substituted alkyl complexes (7). An attempt to substitute **1** with PPh_3 under thermal conditions failed, and an experiment carried out under UV irradiation resulted in the formation of $FvCr_2(CO)_6$ instead of substitution.

When the reaction of **1** was performed with small aliquots of PMe_2Ph added slowly to the reaction mixture, intermediate formation of the methyl-acetyl complex $FvCr(CO)_5(PMe_2Ph)(Me)(COMe)$ (**8**, Scheme 1) could be detected by NMR spectroscopy. Although this compound could not be obtained selectively, it was characterized in situ by NMR spectroscopy. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra are completely compatible with the suggested formulation, with the acetyl group and PMe_2Ph ligands occupying mutually *trans* positions. Thus the ^1H NMR spectrum exhibited CrMe, CrCOMe, and PMe resonances at δ 0.50, 2.38, and 1.96, respectively, in addition to four two-hydrogen fulvalene resonances at δ 4.58, 4.72, 4.86, and 4.93. The $^{13}C\{^1H\}$ NMR spectrum exhibited CrMe, CrCOMe, and PMe resonances at δ −4.8, 49.4 and 18.8, respectively, six fulvalene resonances, three CO resonances, and one MeCO resonance. There is also only a single resonance in the $^{31}P\{^1H\}$ NMR spectrum, confirming the presence of a single geometric isomer.

As indicated in Scheme 1, **8** was also formed by reaction of $Et_4N[FvCr_2(CO)_6Me]$ with first PMe_2Ph, then MeI. As shown, direct addition of PMe_2Ph to the methyl "half" of $Et_4N[FvCr_2(CO)_6Me]$ resulted in the formation of the anionic acetyl compound $Et_4N[FvCr_2(CO)_5(PMe_2Ph)(COMe)]$ (**7**), the IR spectrum of which exhibited carbonyl bands at 1897, 1808, 1789, and 1725 cm^{-1}, similar to those of $(Et_4N)_2[FvCr_2(CO)_6]$, and at 1920, 1837.5, and 1636 (C═O) cm^{-1}, similar to those of **6**; thus **7** presumably assumes the structure shown in Scheme 1, with a *trans* acetyl "half." The ^1H NMR spectrum exhibited a PMe doublet resonance (δ 1.89), an acetyl resonance (δ 2.37), and four fulvalene multiplets (δ 4.23, 4.40, 4.46, and 4.54). The $^{13}C\{^1H\}$ NMR spectrum exhibited single PMe and CO*Me* resonances, as well as six fulvalene, two CO, and one *C*OMe resonance, while the presence of only one resonance in the $^{31}P\{^1H\}$ NMR spectrum confirmed the presence of only a single isomer. As with the other monoanionic complexes **2** and **4**, the $^{13}C\{^1H\}$ NMR spectrum exhibited a large difference (19.7 ppm) between the two bridgehead carbon resonances (δ 92.0 and 111.7).

Contrary to our expectations, addition of an excess of PMe_2Ph to **3** under thermal and photochemical conditions did not result in the formation of a substituted derivative **3**, but rather in decomposition to unidentified precipitates in both cases. The IR spectra indicated the possible formation of trace amounts of a substituted product (1944 and 1869 cm^{-1}), but this reaction was not investigated further.

Consequently, in accord with different substitution behaviours of the homodialkyl compounds **1** and **3**, the mixed alkyl compound **5** reacted with PMe_2Ph only the methyl "half", resulting in the formation in good yield of the mixed alkyl acyl compound $FvCr_2(CO)_5(PMe_2Ph)(CH_2CN)(COMe)$ (**10**) (eq. [6]).

$$[6]\quad \underset{\mathbf{3}}{FvCr_2(CO)_6(CH_2CN)Me} + PMe_2Ph \rightarrow \underset{\mathbf{10}}{\text{trans-}FvCr_2(CO)_4(PMe_2Ph)(CH_2CN)(COMe)}$$

Although the molecular ion of **10** could not be observed in the mass spectrum, the fragmentation pattern is quite consistent with the formulation suggested. The IR spectrum exhibited sets of carbonyl bands at 2019 and 1949 cm^{-1} and at 1922, 1844, and 1639 (C═O) cm^{-1}, similar to those of **4** and **6**, respectively, and suggesting that the acetyl "half" assumes the *trans* isomeric form. The ^1H NMR spectrum exhibited the expected $CrCH_2$ (δ 1.43), PMe (δ 1.98), and COMe (δ 2.40) resonances, as well as four fulvalene resonances (δ 4.70, 4.76, 5.08, 5.22). The $^{13}C\{^1H\}$ NMR spectrum exhibited single $CrCH_2$ (δ −15.3), PMe (δ 18.9), CO*Me* (δ 49.4), and CN (δ 127.6) resonances, as well as six fulvalene resonances (δ 89.2, 91.7, 93.0, 94.0, 101.2, 105.9). three CO resonances (δ 239.8, 249.2, 250.6), and a *C*OMe resonance (δ 271.9).

Earlier it was shown that reduction of *cis,cis*-$FvMo_2(CO)_4L_2Br_2$ (L = PPh_3, PCy_3, PXy_3) with sodium dispersion readily afforded the corresponding dianions (1*b*). Similar treatment of *cis,cis*-$FvCr_2(CO)_4(PMe_2Ph)_2I_2$ (1*d*) was carried out with an excess of sodium dispersion in THF, resulting in the formation of the very air-sensitive salt $Na_2[FvCr_2(CO)_4(PMe_2Ph)_2]$ (eq. [7]).

$$[7]\quad \mathit{cis}\text{,cis-}FvCr_2(CO)_4(PMe_2Ph)_2I_2 + \text{excess Na} \rightarrow Na_2[FvCr_2(CO)_4(PMe_2Ph)_2]$$

This salt was then treated with $ClCH_2CN$ to give **9** in excellent yield (eq. [8]).

$$[8]\quad Na_2[FvCr_2(CO)_4(PMe_2Ph)_2] + 2\ ClCH_2CN \rightarrow \underset{\mathbf{9}}{FvCr_2(CO)_4(PMe_2Ph)_2(CH_2CN)_2}$$

The FAB mass spectrum of **9** exhibited a peak at 723 amu, attributed to the molecular ion plus Na^+, as well as several reasonable fragmentation ions. Consistent with a *trans,trans* structure, the ^1H and $^{13}C\{^1H\}$ spectra are very simple. The former exhibited single $CrCH_2$ (δ 1.23) and PMe (δ 1.91) resonances and only two fulvalene resonances (δ 4.55, 4.58), while the $^{13}C\{^1H\}$ NMR spectrum exhibited a $CrCH_2$ doublet at δ −14.9 (J_{PC} 15 Hz), confirming the presence of a Cr—C bond. In addition, only three fulvalene resonances (δ 88.1, 89.8, 100.5) and one CO carbon doublet (δ 251.6) were observed in the CO region, consistent with the symmetric structure anticipated for the *trans,trans* isomer. No sign of isomerization to *cis,trans* or *cis,cis* forms could be detected in solutions of **9**.

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