Acknowledgment. We are grateful to the CNRS for financial support and for a grant to M.R. and to the Johnson Matthey Technology Center for a generous loan of $PdCl_2$.

Registry No. **1a**, 111026-19-8; **1b**, 111026-20-1; **2a**, 111026-21-2; **2b**, 111026-22-3; **3a**, 111026-26-7; **3b**, 111026-24-5; **4a**, 86028-11-7; **4a**·C_6H_5Cl, 111026-29-0; **4b**, 111026-28-9; **5a**, 111026-27-8; **6a**, 85688-54-6; **7b**, 111026-18-7; $\langle Fe(CO)(NO)_2\rangle_2(\mu\text{-dppm})$, 111026-17-6; $Pd_2FeCl(CO)_2(NO)(\mu\text{-dppm})_2$, 111026-16-5; $[PdPtFe(CO)_2(NO)(THF)(\mu\text{-dppm})_2][PF_6]$, 111059-92-8; $K[Fe(CO)_3NO]$, 25875-19-8; $Pd_2Cl_2(\mu\text{-dppm})_2$, 64345-29-5; $Pd_2Cl_2(\mu\text{-CO})(\mu\text{-dppm}_2)$, 64345-32-0; $\langle Fe(CO)_4\rangle_2(\mu\text{-dppm})$, 52843-17-1; $PdPtCl_2(\mu\text{-dppm})_2$, 82307-36-6; $Na[Mn(CO)_5]$, 13859-41-1; $Mn_2(cO)_{10}$, 10170-69-1; $Mn_2(CO)_8(\mu\text{-dppm})$, 37523-60-7; *fac*-$[MnCl(CO)_3(dppm)]$, 60305-98-8; $Tl[PF_6]$, 60969-19-9; Pd, 7440-05-3; Pt, 7440-06-4; Mn, 7439-96-5; Fe, 7439-89-6.

Supplementary Material Available: Tables of anisotropic thermal parameters (Table S-I), calculated hydrogen atom coordinates (Table S-II), complete bond lengths and angles (Tables S-III and S-IV), and selected weighted least-squares planes for **4a**·C_6H_5Cl (Table S-V) (9 pages); a listing of observed and calculated structure factors for **4a**·C_6H_5Cl (Table S-VI) (26 pages). Ordering information is given on any current masthead page.

Reactions of Transition-Metal σ-Acetylides. 11.[1] Cycloaddition Reactions with 1,1-Dicyano-2,2-bis(trifluoromethyl)ethene. X-ray Structures of $W\{C{=}CPhC(CF_3)_2C(CN)_2\}(CO)_3(\eta\text{-}C_5H_5)$, $Mn\{C{=}CPhC(CF_3)_2C(CN)_2\}(CO)_3(dppe)$, and $Fe\{C{=}CPhC(CF_3)_2C(CN)_2\}(CO)_2(\eta\text{-}C_5H_5)$ and of a Hydration Product, $W\{NH{=}C(OH)C(CN){=}CCPh{=}C(CF_3)_2\}(CO)_2(\eta\text{-}C_5H_5)\cdot H_2O$

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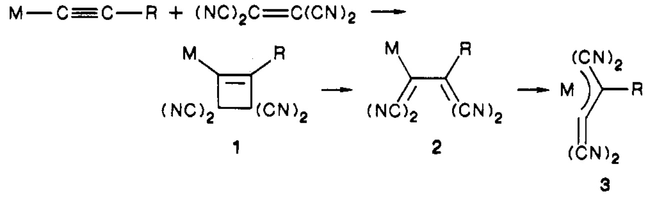
Reactions between $W(C_2Ph)(CO)_3(\eta\text{-}C_5H_5)$ (**6**), $Mn(C_2Ph)(CO)_3(dppe)$ (**7**), or $Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$ (**8**) and $(CF_3)_2C{=}C(CN)_2$ give the corresponding σ-cyclobutenyl complexes, all of which have been fully characterized by X-ray crystallography. The butadienyl complex $Ni\{C[{=}C(CN)_2]CPh{=}C(CF_3)_2\}(PPh_3)(\eta\text{-}C_5H_5)$ (**11**) was obtained from $Ni(C_2Ph)(PPh_3)(\eta\text{-}C_5H_5)$ and the cyanofluoro olefin. Heating **6** in refluxing xylene resulted in ring opening to give $W\{C[{=}C(CN)_2]CPh{=}C(CF_3)_2\}(CO)_3(\eta\text{-}C_5H_5)$ (**9**) and the related allyl complex $W\{\eta^3\text{-}C(CF_3)_2CPhC{=}C(CN)_2\}(CO)_2(\eta\text{-}C_5H_5)$ (**10**). Attempts to prepare **10** by reaction of **6** with Me_3NO gave instead $W\{NH{=}C(OH)C(CN){=}CCPh{=}C(CF_3)_2\}(CO)_2(\eta\text{-}C_5H_5)$ (**12**), confirmed by an X-ray study and formed by addition of H_2O to one of the CN groups, followed by chelation. Crystal data for **6**: monoclinic, space group Pn, $a = 9.575$ (2) Å, $b = 7.493$ (2) Å, $c = 15.670$ (4) Å, $\beta = 103.79$ (2)°, $Z = 2$; 2641 data were refined to $R = 0.075$, $R_w = 0.079$. Crystal data for **7**: orthorhombic, space group $P2_12_12_1$, $a = 11.251$ (2) Å, $b = 17.888$ (3) Å, $c = 19.894$ (3) Å, $Z = 4$; 2947 data were refined to $R = 0.047$, $R_w = 0.050$. Crystal data for **8**: monoclinic, space group $P2_1/a$, $a = 11.430$ (3) Å, $b = 15.201$ (3) Å, $c = 11.887$ (2) Å, $\beta = 102.50$ (2)°, $Z = 4$; 2756 data were refined to $R = 0.044$. Crystal data for **12**: monoclinic, space group $C2/c$, $a = 16.089$ (3) Å, $b = 10.003$ (2) Å, $c = 32.569$ (5) Å, $\beta = 104.2$ (1)°, $Z = 8$; 2433 data were refined to $R = 0.042$, $R_w = 0.047$.

Introduction

A detailed study of the reactions between several transition-metal σ-acetylides and tetracyanoethene [tcne, $C_2(CN)_4$] (Scheme I) has shown that cyclobutenyl (**1**), buta-1,3-dien-2-yl (**2**), and allylic (**3**) complexes are formed from an initial, as yet uncharacterized paramagnetic adduct.[2,3] Some related complexes have been obtained from substituted styrenes $4\text{-}RC_6H_4CH{=}C(CN)(R')$ (R = NO_2 or H; R′ = CN or CO_2Et), one of which was characterized by an X-ray study as **4**. The observed direction of addition of the olefin suggests the intermediacy of a relatively stable dicyanomethide anion, perhaps in a zwitterionic complex such as **5**.[4]

Scheme I. Cycloaddition and Subsequent Reactions of $C_2(CN)_4$ with Transition-Metal Acetylides



This paper describes some of our studies of the related olefin 1,1-dicyano-2,2-bis(trifluoromethyl)ethene [C-

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(1) For part 10 see: Bruce, M. I.; Duffy, D. N.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.*, in press.

(2) Bruce, M. I.; Hambley, T. W.; Snow, M. R.; Swincer, A. G. *Organometallics* **1985**, *4*, 494.

(3) Bruce, M. I.; Hambley, T. W.; Snow, M. R.; Swincer, A. G. *Organometallics* **1985**, *4*, 501.

(4) Bruce, M. I.; Humphrey, P. A.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1986**, *303*, 417.

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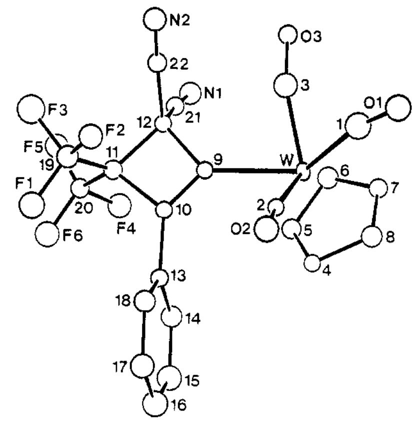

Figure 1. ORTEP view of $\mathrm{W}\{\overline{\mathrm{C}{=}\mathrm{CPhC(CF_3)_2C}}(\mathrm{CN})_2\}(\mathrm{CO})_3(\eta\text{-}\mathrm{C_5H_5})$ (**6**) showing atom-labeling scheme. Atoms not otherwise indicated are carbons.

$(\mathrm{CN})_2{=}\mathrm{C(CF_3)_2}$, dcfe] with σ-acetylide complexes of tungsten, manganese, iron, and nickel. This olefin is readily obtained from malononitrile and hexafluoroacetone,[5] and was chosen because the presence of different electrophilic groups might enable further information to be obtained on the course of these reactions. A reaction involving addition of H_2O across one of the CN groups in the tungsten complex is also reported.

Results and Discussion

Cyclobutenyl Complexes. The reaction between dcfe and $\mathrm{W(C_2Ph)(CO)_3(\eta\text{-}C_5H_5)}$ carried out in dichloromethane afforded the yellow 1:1 adduct **6** in 86% yield. This complex was characterized by elemental microanalysis and from its spectroscopic properties. The IR ν(CO) spectrum (Table I) contained the three-band pattern characteristic of the $\mathrm{W(CO)_3(\eta\text{-}C_5H_5)}$ group, while at higher wavenumbers was a very weak absorption assigned to ν(CN). We have found previously that in the cyclobutenyl isomer, ν(CN) modes are unusually weak.[4] The usual strong ν(CF) bands from the CF_3 groups were found between 1300 and 1100 $\mathrm{cm^{-1}}$ and weak ν(C=C) absorptions at 1612 and 1579 $\mathrm{cm^{-1}}$. The ^{1}H NMR spectrum contained resonances at δ 5.72 (C_5H_5) and 7.4 (Ph) but was otherwise uninformative. The cyclobutenyl formulation was confirmed by an X-ray structure determination (see below).

Similar reactions between dcfe and $\mathrm{Mn(C_2Ph)(CO)_3(dppe)}$ or $\mathrm{Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)}$ also afforded the cyclobutenyl complexes **7** and **8** as white and pale yellow crystalline solids, respectively. For **7**, the ν(CO) band pattern was characteristic of a *fac*-$\mathrm{M(CO)_3}$ group and similar to that found for the phenylethynyl precursor; the ^{1}H NMR spectrum contained a multiplet between δ 1.6 and δ 2.8 (CH_2) and broader resonances between δ 5.2 and δ 7.6 (Ph). Two ν(CO) bands at 2044 and 1995 $\mathrm{cm^{-1}}$ and the sharp singlet at δ 4.95 (C_5H_5) characterized the $\mathrm{Fe(CO)_2(\eta\text{-}C_5H_5)}$ group in **8**. In all cases, the ν(CN), ν(C=C), and ν(CF) absorptions were found at ca 2240, between 1620 and 1550, and between 1300 and 1100 $\mathrm{cm^{-1}}$, respectively.

Molecular Structures of 6–8. Single-crystal X-ray diffraction studies of the three complexes were carried out to determine whether cyclobutenyl or butadienyl ligands were present. Figures 1–3 illustrate the three molecules; Tables II–IV contain atomic coordinates, and Table V collects and compares significant structural data.

The $\mathrm{W(CO)_3(\eta\text{-}C_5H_5)}$, $\mathrm{Mn(CO)_3(dppe)}$, and $\mathrm{Fe(CO)_2(\eta\text{-}C_5H_5)}$ groups are similar to those found in related complexes, such as $\mathrm{W}\{\overline{\mathrm{C}{=}\mathrm{CPhC(CN)_2C}}(\mathrm{CN})_2\}(\mathrm{CO})_3(\eta\text{-}\mathrm{C_5H_5})$,[6] $\mathrm{Mn(C_2\text{-}\mathit{t}\text{-}Bu)(CO)_3(dppe)}$,[7] and $\mathrm{Fe}\{\mathrm{C}[{=}\mathrm{C(CN)_2}]\mathrm{CPh}{=}\mathrm{C(CN)_2}\}(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})$[8] and merit no further comment here. The M–C(sp^2) distances [W, 2.24 (2) Å; Fe, 1.949 (4) Å] compare well with those found in the tungsten [2.202 (9) Å] and iron [1.972 (2) Å] complexes mentioned above. For **7**, this appears to be the first determination of an Mn–C(sp^2) distance [2.099 (7) Å]; this value agrees well with the calculated value (2.07 Å) on the basis of the observed Mn–C(sp) separation in $\mathrm{Mn(C_2\text{-}\mathit{t}\text{-}Bu)(CO)_3(dppe)}$ [1.996 (6) Å] and the difference in C(sp) and C(sp^2) radii (0.07 Å).

Within the cyclobutenyl groups that are similar in all three complexes, the C=C double bonds are normal [1.30 (3)–1.342 (5) Å], but the other three C—C bonds are all somewhat longer than expected, ranging from 1.52 (1) to 1.610 (9) Å. Lengthening of the C—C single bond opposite the C=C double bond has been found in the tcne derivative $\mathrm{W}\{\overline{\mathrm{C}{=}\mathrm{CPhC(CN)_2C}}(\mathrm{CN})_2\}(\mathrm{CO})_3(\eta\text{-}\mathrm{C_5H_5})$ and is related to the ease of cleavage of this bond in conversion to the buta-1,3-dien-2-yl complex $\mathrm{W}\{\mathrm{C}[{=}\mathrm{C(CN)_2}]\mathrm{CPh}{=}\mathrm{C(CN)_2}\}(\mathrm{CO})_3(\eta\text{-}\mathrm{C_5H_5})$.[6] However, in the present complex, the lengthening of C(1)–C(4) contrasts with our previous observation, and we suggest that this feature may be related to the reluctance of these complexes to undergo a

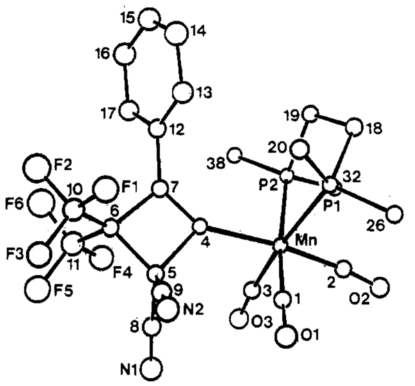

Figure 2. ORTEP view of $\mathrm{Mn}\{\overline{\mathrm{C}{=}\mathrm{CPhC(CF_3)_2C}}(\mathrm{CN})_2\}(\mathrm{CO})_3(\mathrm{dppe})$ (**7**) showing atom-labeling scheme. Atoms not otherwise indicated are carbons. For clarity, only the ipso carbon atoms of the dppe phenyl groups are shown.

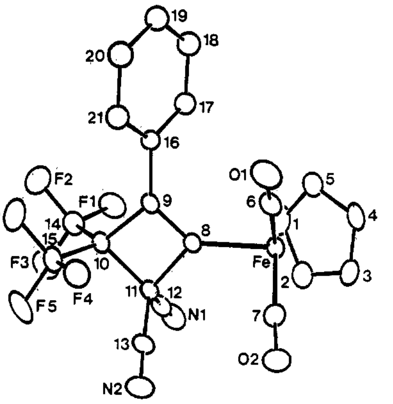

Figure 3. ORTEP view of $\mathrm{Fe}\{\overline{\mathrm{C}{=}\mathrm{CPhC(CF_3)_2C}}(\mathrm{CN})_2\}(\mathrm{CO})_2(\eta\text{-}\mathrm{C_5H_5})$ (**8**) showing atom-labeling scheme. Atoms not otherwise indicated are carbons.

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Table I. IR and NMR Spectroscopic Data for New Compounds

compound	IR[a] (cm^{-1}) ν(CO)	ν(CN)	ν(C=C)	ν(CF)	other bands	^{1}H NMR,[b] δ
$W\{\overline{C{=}CPhC(CF_3)_2C}(CN)_2\}(CO)_3(\eta\text{-}C_5H_5)$ (**6**)	2039, 1960, 1946	2244	1612, 1579	1294 (sh), 1277, 1252, (sh), 1232 (sh), 1222 (sh), 1205	1152 w, 1111 m, 1098 w, 1077 w, 1062 w, 1015 w, 950 m, 940 (sh), 844 m, 819 w, 770 w, 723 m, 710 w, 700 w, 630 w	5.72 (s, 5 H, C_5H_5), 7.4 (m, 5 H, Ph)
$Mn\{\overline{C{=}CPhC(CF_3)_2C}(CN)_2\}(CO)_3(dppe)$ (**7**)	2109, 1943 (br)	2241	1610, 1590, 1578, 1555	1290 (sh), 1272, 1250 w, 1218 w, 1197	1482 w, 1440 m, 1308 w, 1181 (sh), 1109 m, 941 w, 740 w, 722 w, 707 m, 688 m, 676 w, 662 w, 630 w	1.6–2.8 (m, 4 H, CH_2), 5.22 (d, J = 8 Hz, 2 H, Ph), 6.61 (t, J = 7 Hz, 2 H, Ph), 7.00 (t, J = 7 Hz, 1 H, Ph), 7.6 (m, 20 H, PhP)
$Fe\{\overline{C{=}CPhC(CF_3)_2C}(CN)_2\}(CO)_2(\eta\text{-}C_5H_5)$ (**8**)	2044, 1995	2243	1615, 1590, 1580	1275, 1222 (sh), 1212 (sh), 1200, 1190 (sh), 1155 m, 1110	1440 m, 1425 m, 1370 (sh), 1320 (sh), 1300 (sh), 1160 w, 1079 m, 1060 m, 1035 m, 1020 m, 1010 m, 970 (sh), 950 s, 934 s, 885 w, 858 s, 843 m, 840 m, 817 s, 800 (sh), 772 s, 755 m, 722 s, 710 m, 696 s, 675 w, 658 (sh), 640 m, 620 w	4.95 (s, 5 H, C_5H_5), 7.3 (m, 5 H, Ph)
$W\{C[{=}C(CN)_2]CPh{=}C(CF_3)_2\}(CO)_3(\eta\text{-}C_5H_5)$ (**9**)	2044, 1972, 1950	2219 w	1626, 1622, 1616	1254, 1255 m, 1210 m, 1161	1448 w, 1336 m, 1138 w, 1121 w, 1080 w, 1063 m, 1015 w, 1002 w, 966 m, 883 w, 868 w, 860 (sh), 846 m, 824 w, 773 w, 756 w, 730 w, 721 (sh), 710 w, 700 m	5.30 (s, 5 H, C_5H_5), 7.4 (m, 5 H, Ph)
$W\{\eta^3\text{-}C(CF_3)_2CPhC{=}C(CN)_2\}(CO)_2(\eta\text{-}C_5H_5)$ (**10**)	2052, 2004	2219 m	1579, 1575 m, 1567	1295 m, 1266 w, 1234 m, 1210 w, 1195, 1186 m, 1140	1498 w, 1475 w, 1427 m, 1388 w, 1344 m, 1056 w, 1001 m, 937 m, 914 m, 890 w, 855 w, 821 w, 780 w, 759 w, 747 m	5.79 (s, 5 H, C_5H_5), 7.3 (m, 5 H, Ph)
$Ni\{C[{=}C(CN)_2]CPh{=}C(CF_3)_2\}(PPh_3)(\eta\text{-}C_5H_5)$ (**11**)		2220 m (Nujol)	1620 m, 1600 w	1332, 1252, 1215, 1167 m, 1157	1439 (sh), 1190 w, 1145 (sh), 1110 w, 1094 m, 1060 m, 1022 w, 1003 w, 967 m, 920 w, 862 w, 840 m, 830 w, 816 m, 803 m, 780 w, 749 m, 727 w, 717 w, 702 s, 648 w	5.30 (m, 5.5 H, C_5H_5 + $0.25CH_2Cl_2$), 7.2 (m, 20 H, Ph)
$W\{\overline{NH{=}C(OH)C(CN){=}C}CPh{=}C(CF_3)_2\}(CO)_2(\eta\text{-}C_5H_5)$ (**12**)	1976, 1903	2230, 2208, 1650 s	1546	1334, 1250, 1231 (sh), 1215 m, 1158, 1150	2730 w, 1619 w, 1614 w, 1133 w, 1064 m, 982 s, 867 w, 842 m, 831 m, 739 w, 714 w, 703 s	4.91 (s, 5 H, C_5H_5), 5.30 (s, 0.5 H, CH_2Cl_2), 7.4 (m, 5 H, Ph)

[a] The bands reported for carbonyl and CF_3 groups are strong unless noted otherwise, and the CN bands are very weak. Carbonyl and CN bands were recorded on dichloromethane solutions; all other bands were recorded as Nujol mulls. [b] Chemical shifts are reported upfield of TMS, in ppm.

related ring-opening reaction. Angles at the C(sp^2) carbons within the cyclobutenyl ring range from 89.6 (5) to 99.0 (5)° and angles at the C(sp^3) carbons, from 84 (2) to 87 (2)°.

As revealed by structural studies, dcfe adds to the three phenylethynyl complexes in a preferred direction so that the $C(CN)_2$ group becomes attached to the α-carbon of the acetylide. We have obtained no evidence for the formation of the isomer that would be produced by addition in the reverse direction. While these findings may be the result of the bulk of the CF_3 groups directing the addition in this way, we are more inclined to view these results as being consistent with our earlier suggestion that an intermediate may be stabilized by delocalization of charge over the dicyanomethylene group, rather than on the $C(CF_3)_2$ group. Such a proposal is consistent with the known stability of cyanocarbon anions and was first suggested in regard to the tcne/$Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$ reaction by Davison and Solar.[9] In the latter case, however, we have shown earlier that their proposed zwitterionic complex is in fact the σ-cyclobutenyl derivative.[8]

In the present complexes, the geometry of the cyclobutenyl ligands, formed by ring closure of the zwitterionic ligand, with their long C–C bonds, suggests that the dicyanomethylene group continues to withdraw electron density onto itself.

Butadienyl Complexes. A feature of the chemistry of the σ-cyclobutenyl complexes derived from tcne is their isomerization to the corresponding butadienyl complexes **2** (Scheme I), which is often so rapid as to preclude isolation of the cyclobutenyl derivatives. The analogous complexes derived from dcfe isomerize much less readily. In the case of **6**, for example, heating for about 3 h in refluxing xylene afforded $W\{C[{=}C(CN)_2]CPh{=}C(CF_3)_2\}(CO)_3(\eta\text{-}C_5H_5)$ (**9**) (8%) together with the allylic complex $W\{\eta^3\text{-}C(CN)_2CPhC{=}C(CF)_3)_2\}(CO)_2(\eta\text{-}C_5H_5)$ (**10**), obtained in 26% yield. These compounds were identified from their IR ν(CO) spectra and from their mass spectra, which contained $[M]^+$ ions at m/z 648 and 620, respectively.

The reaction between dcfe and $Ni(C_2Ph)(PPh_3)(\eta\text{-}C_5H_5)$ was carried out in refluxing benzene and afforded $Ni\{C[{=}C(CN)_2]CPh{=}C(CF_3)_2\}(PPh_3)(\eta\text{-}C_5H_5)$ (**11**) directly, the intermediate cyclobutenyl complex not being detected. No

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(9) Davison, A.; Solar, J. P. *J. Organomet. Chem.* **1979**, *166*, C13.

Table II. Fractional Atomic Coordinates ($\times 10^5$ for W; $\times 10^4$ for Other Atoms) for $W\{\overline{C{=}CPhC(CF_3)_2C}(CN)_2\}_3(\eta\text{-}C_5H_5)$ (6)

atom	*x*	*y*	*z*
W	00000 (...)	−20498 (7)	00000 (...)
C(1)	1096 (39)	9 (56)	−367 (22)
O(1)	1921 (28)	1088 (40)	−430 (17)
C(2)	−1139 (18)	59 (26)	161 (13)
O(2)	−1634 (23)	1424 (34)	342 (14)
C(3)	−52 (49)	−2327 (54)	−1239 (28)
O(3)	304 (29)	−2925 (24)	−1899 (17)
C(4)	−4 (27)	−2989 (26)	1344 (17)
C(5)	−152 (24)	−4586 (37)	873 (14)
C(6)	1076 (28)	−4841 (42)	440 (16)
C(7)	2029 (28)	−3426 (38)	792 (16)
C(8)	1486 (34)	−2350 (41)	1327 (21)
C(9)	−2297 (24)	−2778 (27)	−588 (14)
C(10)	−3468 (23)	−2733 (25)	−303 (14)
C(11)	−4437 (25)	−3577 (34)	−1145 (15)
C(12)	−3009 (20)	−3690 (29)	−1444 (12)
C(19)	−5573 (38)	−2312 (40)	−1628 (22)
C(20)	−5201 (24)	−5328 (36)	−1023 (15)
F(1)	−6644 (30)	−2052 (23)	−1257 (17)
F(2)	−5031 (18)	−738 (25)	−1767 (12)
F(3)	−6202 (35)	−2954 (27)	−2458 (21)
F(4)	−4224 (22)	−6423 (33)	−491 (13)
F(5)	−5589 (21)	−6169 (30)	−1755 (12)
F(6)	−6242 (20)	−5189 (31)	−607 (12)
C(21)	−2445 (22)	−5442 (33)	−1547 (13)
N(1)	−1834 (36)	−6815 (38)	−1584 (21)
C(22)	−2997 (29)	−2782 (28)	−2316 (17)
N(2)	−2962 (36)	−2001 (30)	−2910 (21)
C(14)	−3682 (22)	−3431 (17)	1223 (11)
C(15)	−4063 (22)	−2971 (17)	1999 (11)
C(16)	−4650 (22)	−1295 (17)	2083 (11)
C(17)	−4855 (22)	−79 (17)	1391 (11)
C(18)	−4474 (22)	−539 (17)	614 (11)
C(13)	−3887 (22)	−2215 (17)	530 (11)

reaction occurred at ambient temperatures. However, it is worth noting that this complex was the only tractable material obtained from a complex and rather unstable reaction product. Characterization of **11** rests on the IR distinction between the two isomeric species established earlier and confirmed in the case of the tungsten isomers **6** and **9**, namely, a weak ν(CN) absorption at ca. 2220 cm^{-1} for the dienyl ligand compared with very weak absorptions found for the cyclobutenyls. In addition, the fragmentation pattern of the molecular ion (FAB MS) did not include loss of dcfe (see below).

A structural feature of the cyclobutenyl complexes derived from tcne or $CH(C_6H_4NO_2\text{-}4){=}C(CN)_2$ is the long C—C bond opposite the C=C doubld bond in the four-membered ring; at ca. 1.60 Å, it is already predisposed to the ring-opening isomerization. As shown below, the four-membered rings in complexes **6–8** do not share this feature, and the relative difficulty of the ring-opening reaction can, in part at least, be ascribed to the stronger C–C bond. We note also that there is an apparent electron deficiency (as revealed by bond lengthening) in the C(1)–C(4) bonds, and this too would preclude the electron transfer which occurs during the ring opening.

The second product obtained after heating **6** was identified as the allylic complex **10**. Again, a contrast is found between the reactions of the tcne- and the dcfe-derived complexes: the former require irradiation in order to expel the CO ligand efficiently, the thermal reaction affording the allyl in very low yield, whereas **10** is the major product from heating **6**.

Hydrolysis of 6: Synthesis and Structure of $\overline{W\{NH{=}C(OH)C(CN){=}C}CPh{=}C(CF_3)_2\}(CO)_2(\eta\text{-}C_5H_5)$ (12). In an attempt to convert **6** to an allylic derivative, the complex was treated with trimethylamine oxide ($Me_3NO{\cdot}2H_2O$) in acetone to give an orange crystalline product (**12**) in 24% yield. The IR spectrum contains two ν(CO) bands and a strong ν(CN) absorption, together with several bands between 3380 and 3000 cm^{-1} which suggested the presence of NH or OH groups. No resonances attributable to these groups were found in the ^{1}H NMR spectrum. Microanalytical data were consistent with a formulation derived from **6** by loss of a CO ligand and addition of H_2O; the FAB mass spectrum also supported this interpretation. The molecular structure of **12** was determined by X-ray methods and is illustrated by Figure 4; Table VI lists the atomic coordinates and Table VII bond distances and angles.

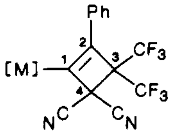
Table III. Fractional Atomic Coordinates ($\times 10^5$ for Mn, $\times 10^4$ for Other Atoms) for $Mn\{\overline{C{=}CPhC(CF_3)_2C}(CN)_2\}(CO)_3(dppe)$ (7)

atom	*x*	*y*	*z*
Mn	54890 (9)	42038 (5)	20667 (4)
P(1)	3699 (2)	3571 (1)	2230 (1)
P(2)	6172 (2)	3041 (1)	1693 (1)
N(1)	7729 (7)	5871 (4)	2922 (4)
N(2)	4809 (7)	5515 (4)	4062 (4)
F(1)	5653 (7)	4034 (3)	4721 (2)
F(2)	7346 (8)	3645 (4)	5027 (3)
F(3)	6973 (6)	4815 (3)	5015 (2)
F(4)	8978 (4)	4308 (3)	3310 (3)
F(5)	8924 (6)	4935 (3)	4226 (3)
F(6)	9133 (6)	3754 (4)	4246 (4)
O(1)	4313 (6)	5606 (3)	2475 (3)
O(2)	4766 (5)	4586 (3)	683 (3)
O(3)	7680 (5)	4968 (3)	1602 (3)
C(1)	4767 (6)	5065 (4)	2333 (3)
C(2)	5025 (6)	4399 (4)	1213 (4)
C(3)	6860 (7)	4659 (4)	1819 (3)
C(4)	6194 (6)	4082 (3)	3037 (3)
C(5)	6572 (7)	4787 (4)	3493 (3)
C(6)	7217 (7)	4204 (4)	3960 (3)
C(7)	6674 (7)	3623 (4)	3493 (3)
C(8)	7258 (7)	5382 (4)	3179 (4)
C(9)	5558 (8)	5181 (4)	3812 (4)
C(10)	6802 (11)	4181 (6)	4685 (4)
C(11)	8593 (8)	4300 (5)	3926 (6)
C(13)	5641 (4)	2439 (3)	3755 (3)
C(14)	5637 (4)	1678 (3)	3907 (3)
C(15)	6702 (4)	1279 (3)	3917 (3)
C(16)	7770 (4)	1641 (3)	3774 (3)
C(17)	7774 (4)	2402 (3)	3622 (3)
C(12)	6709 (4)	2801 (3)	3612 (3)
C(18)	3827 (7)	2650 (4)	1812 (4)
C(19)	5070 (6)	2329 (4)	1913 (3)
C(21)	2504 (5)	2706 (3)	3196 (2)
C(22)	2011 (5)	2587 (3)	3831 (2)
C(23)	2125 (5)	3130 (3)	4329 (2)
C(24)	2734 (5)	3793 (3)	4194 (2)
C(25)	3227 (5)	3912 (3)	3560 (2)
C(20)	3113 (5)	3369 (3)	3061 (2)
C(27)	1625 (4)	4450 (3)	2183 (2)
C(28)	679 (4)	4805 (3)	1862 (2)
C(29)	520 (4)	4722 (3)	1170 (2)
C(30)	1307 (4)	4283 (3)	800 (2)
C(31)	2254 (4)	3927 (3)	1120 (2)
C(26)	2412 (4)	4010 (3)	1812 (2)
C(33)	5454 (4)	2616 (3)	373 (2)
C(34)	5542 (4)	2643 (3)	−327 (2)
C(35)	6467 (4)	3040 (3)	−629 (2)
C(36)	7303 (4)	3409 (3)	−232 (2)
C(37)	7216 (4)	3382 (3)	467 (2)
C(32)	6291 (4)	2985 (3)	769 (2)
C(39)	8536 (4)	3091 (2)	2116 (3)
C(40)	9644 (4)	2778 (2)	2258 (3)
C(41)	9813 (4)	2009 (2)	2197 (3)
C(42)	8875 (4)	1552 (2)	1994 (3)
C(43)	7767 (4)	1864 (2)	1852 (3)
C(38)	7598 (4)	2634 (2)	1914 (3)

Table IV. Fractional Atomic Coordinates ($\times10^5$ for Fe, $\times10^4$ for Other Atoms) for $\mathrm{Fe\{\overline{C{=}CPhC(CF_3)_2C}(CN)_2\}(CO)_2(\eta\text{-}C_5H_5)}$ (8)

atom	*x*	*y*	*z*
Fe	18882 (6)	39468 (4)	34244 (5)
C(1)	951 (5)	3598 (3)	1756 (4)
C(2)	158 (5)	3595 (3)	2532 (5)
C(3)	603 (5)	2957 (3)	3414 (5)
C(4)	1644 (6)	2583 (3)	3180 (5)
C(5)	1874 (6)	2983 (3)	2153 (5)
C(6)	3452 (5)	3882 (3)	4037 (4)
O(1)	4443 (3)	3846 (3)	4442 (3)
C(7)	1560 (4)	4374 (3)	4708 (4)
O(2)	1354 (3)	4604 (3)	5555 (3)
C(8)	2167 (3)	5098 (2)	2809 (3)
C(9)	2998 (3)	5483 (3)	2332 (3)
C(10)	2394 (4)	6388 (3)	2144 (3)
C(11)	1368 (3)	5953 (3)	2683 (3)
C(12)	184 (4)	5835 (3)	1905 (4)
C(13)	1182 (4)	6333 (3)	3772 (4)
C(14)	3060 (5)	7141 (3)	2893 (5)
C(15)	1993 (5)	6670 (3)	891 (5)
C(17)	4013 (2)	4443 (2)	1267 (3)
C(18)	5043 (2)	4094 (2)	990 (3)
C(19)	6161 (2)	4461 (2)	1460 (3)
C(20)	6248 (2)	5178 (2)	2206 (3)
C(21)	5217 (2)	5527 (2)	2483 (3)
C(16)	4100 (2)	5160 (2)	2014 (3)
N(1)	−722 (4)	5706 (3)	1324 (4)
N(2)	1057 (4)	6601 (3)	4619 (4)
F(1)	3495 (3)	6873 (2)	3960 (3)
F(2)	3984 (3)	7421 (2)	2479 (3)
F(3)	2350 (3)	7822 (2)	2934 (3)
F(4)	1505 (3)	5998 (2)	233 (2)
F(5)	1179 (3)	7307 (2)	758 (3)
F(6)	2907 (3)	6952 (2)	461 (3)

Table V. Selected Bond Lengths (Å) and Angles (deg) for Complexes 6–8



parameter	compound 6	7	8
M–C(1)	2.24 (2)	2.099 (7)	1.949 (4)
C(1)–C(2)	1.30 (3)	1.337 (9)	1.342 (5)
C(2)–C(3)	1.56 (3)	1.52 (1)	1.534 (5)
C(3)–C(4)	1.55 (3)	1.58 (1)	1.596 (6)
C(1)–C(4)	1.52 (3)	1.610 (9)	1.577 (5)
C(2)–C(1)–C(4)	94 (2)	89.6 (5)	92.8 (3)
C(1)–C(2)–C(3)	95 (2)	99.0 (5)	96.6 (3)
C(2)–C(3)–C(4)	84 (2)	84.7 (5)	85.2 (3)
C(1)–C(4)–C(3)	87 (2)	86.3 (5)	85.4 (3)

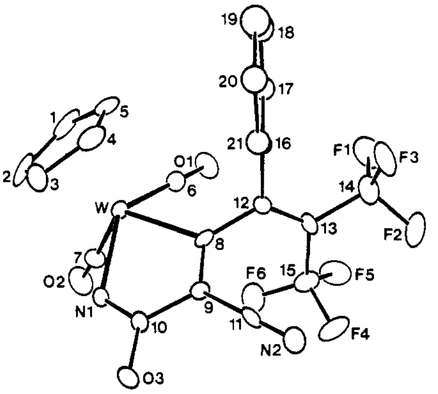
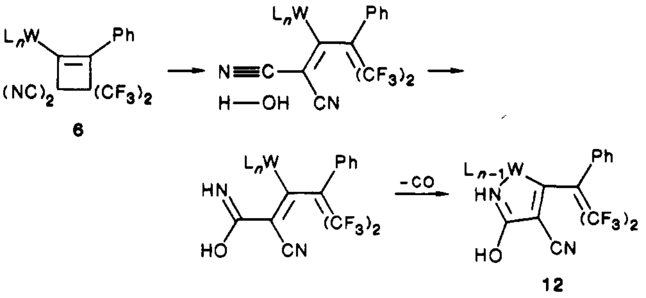


Figure 4. ORTEP view of $\mathrm{\overline{W\{NH{=}C(OH)C(CN){=}C}CPh{=}C(CF_3)_2\}(CO)_2(\eta\text{-}C_5H_5)}$ (12) showing atom-labeling scheme. Atoms not otherwise indicated are carbons.

Table VI. Fractional Atomic Coordinates ($\times10^5$ for W, $\times10^4$ for Other Atoms) for $\mathrm{\overline{W\{NH{=}C(OH)C(CN){=}C}CPh{=}C(CF_3)_2\}(CO)_2(\eta\text{-}C_5H_5)\bullet H_2O}$ (12)

atom	*x*	*y*	*z*
W	−8340 (3)	−6030 (5)	−11887 (1)
C(1)	−654 (14)	−2539 (16)	−1518 (8)
C(2)	−261 (11)	−2736 (14)	−1088 (10)
C(3)	−897 (13)	−2731 (16)	−862 (6)
C(4)	−1707 (10)	−2510 (13)	−1183 (6)
C(5)	−1561 (12)	−2383 (13)	−1577 (5)
C(6)	−976 (8)	313 (13)	−1749 (5)
O(1)	−1042 (7)	833 (11)	−2066 (3)
C(7)	337 (9)	130 (16)	−1102 (5)
O(2)	1024 (7)	536 (12)	−1085 (4)
C(8)	−1811 (7)	822 (10)	−1151 (4)
C(9)	−1840 (6)	1153 (11)	−743 (3)
C(10)	−1142 (7)	648 (11)	−412 (4)
C(11)	−2486 (7)	1962 (13)	−627 (3)
N(1)	−591 (5)	−26 (9)	−536 (3)
N(2)	−2996 (7)	2572 (13)	−529 (3)
O(3)	−1055 (6)	927 (12)	3 (3)
C(12)	−2506 (6)	1289 (12)	−1503 (4)
C(13)	−2572 (7)	2531 (13)	−1663 (4)
C(14)	−3334 (9)	2960 (16)	−2001 (5)
C(15)	−1919 (10)	3593 (13)	−1499 (5)
F(1)	−3210 (6)	2856 (14)	−2385 (3)
F(2)	−3535 (8)	4254 (10)	−1959 (5)
F(3)	−4052 (5)	2361 (11)	−2010 (3)
F(4)	−2133 (7)	4429 (8)	−1232 (4)
F(5)	−1832 (8)	4367 (8)	−1828 (3)
F(6)	−1154 (5)	3132 (9)	−1326 (3)
C(16)	−3195 (6)	−323 (9)	−2075 (3)
C(17)	−3742 (6)	−1393 (9)	−2224 (3)
C(18)	−4234 (6)	−1949 (9)	−1969 (3)
C(19)	−4178 (6)	−1437 (9)	−1565 (3)
C(20)	−3631 (6)	−367 (9)	−1416 (3)
C(21)	−3140 (6)	190 (9)	−1670 (3)
O(s)	588 (30)	3787 (57)	−317 (17)

Scheme II. Hydrolysis of Complex 6



The tungsten atom is coordinated by two CO groups [W–CO = 2.003 (17), 1.976 (15) Å] and a C_5H_5 ligand [W–C(cp) = 2.267 (14)–2.394 (16) Å, average 2.335 Å], together with carbon and nitrogen atoms of a chelating 1-hydroxy-1-imido-2-cyano-4-phenyl-5,5-bis(trifluoromethyl)penta-2,4-dien-3-yl ligand [W–N = 2.145 (8) Å; W–C = 2.148 (10) Å]. The W–C(8) bond is 0.1 Å shorter than that found in the precursor 6. The ligand is related to the cyclobutenyl ligand originally present in 6 by ring opening [cleavage of C(11)–C(12)] and addition of a molecule of water across one of the CN groups. The resulting imido function displaces a CO group to give a five-membered $\overline{\mathrm{W{-}N{=}C{-}C{=}C}}$ chelate ring. This is represented in Scheme II, although we cannot establish at which stage the cyclobutenyl ring is cleaved to form the butadienyl group.

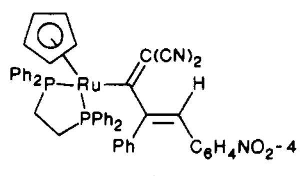
The reaction contrasts with the usual behaviour of polycyano olefins toward water. Tetracyanoethene, for ex-

Table VII. Bond Lengths (Å) and Angles (deg) for Complex 12

	Bond Distances		
W-C(1)	2.267 (14)	W-C(6)	2.003 (17)
W-C(2)	2.316 (13)	W-C(7)	1.976 (15)
W-C(3)	2.394 (16)	W-C(8)	2.148 (10)
W-C(4)	2.372 (13)	W-N(1)	2.145 (8)
W-C(5)	2.326 (14)		
C(6)-O(1)	1.140 (17)	C(7)-O(2)	1.166 (17)
C(8)-C(9)	1.381 (16)	C(8)-C(12)	1.467 (16)
C(12)-C(13)	1.342 (16)	C(12)-C(21)	1.507 (14)
C(13)-C(14)	1.496 (17)	C(13)-C(15)	1.498 (17)
C(14)-F(1)	1.317 (17)	C(15)-F(4)	1.313 (15)
C(14)-F(2)	1.349 (18)	C(15)-F(5)	1.357 (16)
C(14)-F(3)	1.295 (16)	C(15)-F(6)	1.305 (16)
C(9)-C(10)	1.443 (16)	C(9)-C(11)	1.439 (15)
C(10)-O(3)	1.353 (16)	C(11)-N(2)	1.130 (13)
C(10)-N(1)	1.256 (12)		
	Bond Angles		
C(1)-W-C(2)	35.6 (7)	C(1)-W-C(3)	58.3 (7)
C(1)-W-C(4)	57.4 (6)	C(1)-W-C(5)	36.3 (6)
C(1)-W-C(6)	87.7 (7)	C(1)-W-C(7)	99.0 (6)
C(1)-W-C(8)	140.8 (7)	C(1)-W-N(1)	133.3 (7)
C(2)-W-C(3)	34.6 (7)	C(2)-W-C(4)	58.3 (6)
C(2)-W-C(5)	60.1 (6)	C(2)-W-C(6)	120.2 (8)
C(2)-W-C(7)	89.4 (6)	C(2)-W-C(8)	151.1 (6)
C(2)-W-N(1)	98.0 (8)	C(3)-W-C(4)	36.0 (5)
C(3)-W-C(5)	59.4 (6)	C(3)-W-C(6)	143.5 (6)
C(3)-W-C(7)	114.2 (6)	C(3)-W-C(8)	116.9 (6)
C(3)-W-N(1)	79.4 (5)	C(4)-W-C(5)	33.8 (5)
C(4)-W-C(6)	116.1 (6)	C(4)-W-C(7)	147.5 (6)
C(4)-W-C(8)	95.2 (4)	C(4)-W-N(1)	99.9 (5)
C(5)-W-C(6)	85.7 (5)	C(5)-W-C(7)	134.1 (6)
C(5)-W-C(8)	105.2 (5)	C(5)-W-N(1)	133.6 (4)
C(6)-W-C(7)	81.5 (6)	C(6)-W-C(8)	80.0 (4)
C(6)-W-N(1)	137.1 (5)	C(7)-W-C(8)	115.5 (5)
C(7)-W-N(1)	79.8 (5)	C(8)-W-N(1)	73.9 (4)
C(1)-C(2)-C(3)	109 (2)	C(2)-C(3)-C(4)	105 (2)
C(3)-C(4)-C(5)	111 (2)	C(4)-C(5)-C(1)	106 (2)
C(5)-C(1)-C(2)	110 (2)	W-C(6)-O(1)	179 (1)
W-C(7)-O(2)	175 (1)	W-C(8)-C(9)	114.4 (8)
W-C(8)-C(12)	126.5 (8)	W-N(1)-C(10)	119.4 (7)
N(1)-C(10)-O(3)	122 (1)	N(1)-C(10)-C(9)	116 (1)
O(3)-C(10)-C(9)	123.0 (9)	C(8)-C(9)-C(10)	115.5 (9)
C(8)-C(9)-C(11)	126 (1)	C(10)-C(9)-C(11)	118.7 (9)
C(9)-C(11)-N(2)	178 (1)	C(9)-C(8)-C(12)	118.4 (9)
C(8)-C(12)-C(13)	125 (1)	C(8)-C(12)-C(21)	111.6 (9)
C(13)-C(12)-C(21)	124 (1)	C(12)-C(13)-C(14)	122 (1)
C(12)-C(13)-C(15)	122 (1)	C(14)-C(13)-C(15)	116 (1)
C(13)-C(14)-F(1)	113 (1)	C(13)-C(15)-F(4)	114 (1)
C(13)-C(14)-F(2)	112 (1)	C(13)-C(15)-F(5)	109 (1)
C(13)-C(14)-F(3)	117 (1)	C(13)-C(15)-F(6)	114 (1)
F(1)-C(14)-F(2)	106 (1)	F(4)-C(15)-F(5)	105 (1)
F(1)-C(14)-F(3)	106 (1)	F(4)-C(15)-F(6)	108 (1)
F(2)-C(14)-F(3)	102 (1)	F(5)-C(15)-F(6)	106 (1)

ample, reacts with water to give tricyanoethenol (at low pH) or pentacyanopropenide ion (at high pH).[10] A brief communication describes addition of water to one of the CN groups (5000–6700 atm, 110–150 °C) to give 2,3,3-tricyanoacrylamide, $C(CN)_2{=}C(CN)C(O)NH_2$,[11] but this reaction pathway does not seem to have been further substantiated. However, our reaction has a precedent in the observations of King and Saran,[12] who described the formation of $M\{NH{=}C(OH)C(CN){=}CH\}(CO)_2(\eta\text{-}C_5H_5)$ (M = Mo or W) (**13**) when the 1-chloro-2,2-dicyanovinyl complexes $M\{CCl{=}C(CN)_2\}(CO)_3(\eta\text{-}C_5H_5)$ were treated with alumina containing adsorbed water.

Mass Spectral Studies. The utility of the fast atom bombardment (FAB) technique to obtain mass spectra of thermally sensitive, involatile, or ionic organometallic compounds has been reviewed.[13] Application of this method to the analysis of the isomeric cyclobutenyl and butadienyl complexes shows that a characteristic breakdown pathway of carbonyl-free ions of the type $[M\{C{=}CPhC(CF_3)_2C(CN)_2\}]^+$ is loss of $C_2(CF_3)_2(CN)_2$ in a reaction which is essentially the reverse of the synthetic procedure. This route is not found for corresponding ions in the isomeric butadienyl complexes, which is not unexpected, since the C=C double bond originally present in the olefin has been cleaved in these derivatives.



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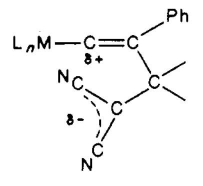

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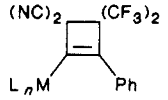
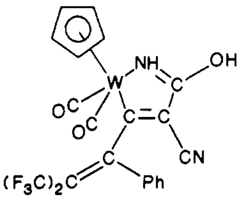


6: $ML_n = W(CO)_3(\eta\text{-}C_5H_5)$
7: $ML_n = Mn(CO)_3(dppe)$
8: $ML_n = Fe(CO)_2(\eta\text{-}C_5H_5)$



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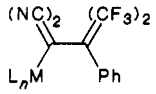
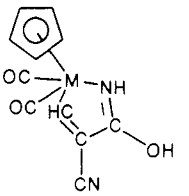
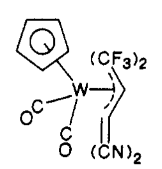


9: $ML_n = W(CO)_3(\eta\text{-}C_5H_5)$
11: $ML_n = Ni(PPh_3)(\eta\text{-}C_5H_5)$



13, M = Mo, W



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Thus, comparison of the FAB mass spectra of the tungsten complexes **6** and **9** shows that while the spectra of both complexes contained strong $[M - nCO]^+$ ions (n = 0–3), that of **6** also contains $[M - 3CO - dcfe]^+$ (m/z 350), not found in the spectrum of **9**. Similar differences in the fragmentation patterns of the tcne complexes $Mn(R_{CN})(CO)_3(dppe)$ [$R_{CN} = C{=}CPhC(CN)_2C(CN)_2$ and $C\{=C(CN)_2\}CPh{=}C(CN)_2$] have been described by us elsewhere.[1] While we have not been able to compare them with those of the diene isomers, the spectra of **7** and **8** both contain strong ions formed by loss of dcfe from $[M - 3CO]^+$ (for **7**) or $[M - 2CO]^+$ (for **8**). By this criterion, we have assigned the butadienyl structure **11** to the nickel complex described above, since there is no ion formed by loss of dcfe in its FAB mass spectrum.

Other features of the mass spectra of these complexes include loss of one CF_3 group from the $M\{C{=}CPhC(CF_3)_2C(CN)_2\}$-containing ions from cyclobutenyl complexes, but not from the open ligand. In addition, loss of F (from CF_3 groups) and transfer of F to the metal occur. In the tungsten complexes, several ditungsten ions, such as $[W_2F(C_5H_5)_2]^+$, are found, presumably as a result of ion–molecule association reactions.

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Table VIII. Crystal and Intensity Collection Data for Complexes 6–8 and 12

	6	7	8	12
formula	$C_{22}H_{10}F_6N_2O_3W$	$C_{43}H_{29}F_6MnN_2O_3P_2$	$C_{21}H_{10}F_6FeN_2O_2$	$C_{21}H_{12}F_6N_2O_3W,H_2O$
M_r	648.2	852.6	492.2	656.2
cryst system	monoclinic	orthorhombic	monoclinic	monoclinic
space group	Pn	$P2_12_12_1$	$P2_1/a$	$C2/c$
	(variant C_s^2, No. 7)	(D_2^4, No. 19)	(variant C_{2h}^5, No. 14)	(C_{2h}^6, No. 15)
a, Å	9.575 (2)	11.251 (2)	11.430 (3)	16.089 (3)
b, Å	7.493 (2)	17.888 (3)	15.201 (3)	10.003 (2)
c, Å	15.670 (4)	19.894 (3)	11.887 (2)	32.569 (5)
β, deg	103.79 (2)	90	102.50 (2)	104.2 (1)
U, Å^3	1091.9	4003.8	2016.4	5081.4
D_{measd}, g cm^{-3}	1.97	1.42	1.61	1.75
Z	2	4	4	8
D_{calcd}, g cm^{-3}	1.972	1.415	1.621	1.718
μ, cm^{-1}	54.44	4.26	7.83	46.82
max/min transmission factors	0.3624/0.1827	0.9168/0.8673	N/A	0.6772/0.3171
F(000)	616	1736	984	2520
θ range, deg	1–25	1–22.5	1–25	1–22.5
reflns measd	3585	3542	3846	5437
unique reflns	2875	3429	3414	3309
criterion of observability	$3.0\sigma(I)$	$2.5\sigma(I)$	$2.5\sigma(I)$	$2.5\sigma(I)$
obsd reflns	2641	2947	2756	2433
R	0.075	0.047	0.044	0.042
k	0.99	5.13	na[a]	1.0
g	0.0081	0.0001	na[a]	0.0038
R_w	0.079	0.050	na[a]	0.047

[a] na = not available.

Experimental Section

General Conditions. All reactions were run under nitrogen; no special precautions were taken to exclude air during workup, since most complexes proved to be stable in air as solids and for short times in solution. Microanalyses were by the Canadian Microanalytical Service, Vancouver, British Columbia, Canada.

Instruments: Perkin-Elmer 683 double-beam spectrometer, NaCl optics (IR); Bruker WP80 spectrometer (^{1}H NMR at 80 MHz, ^{13}C NMR at 20.1 MHz); GEC-Kratos MS3074 mass spectrometer (mass spectra at 70-eV ionizing energy, 4-kV accelerating potential).

FAB mass spectra were obtained on a VG ZAB 2HF instrument equipped with a FAB source. Argon was used as the exciting gas, with source pressures typically 10^{-6} mbar; the FAB gun voltage was 7.5 kV, current 1 mA. The ion accelerating potential was 8 kV. The matrix was 3-nitrobenzyl alcohol. The complexes were made up as ca. 0.5 M solutions in acetone or dichloromethane; a drop was added to a drop of matrix, and the mixture was applied to the FAB probe tip. Spectra are reported below in the form: m/z, assignment, relative intensity; multiisotopic species are normalized on the most abundant metal isotopes, ^{56}Fe, ^{58}Ni, and ^{184}W. Peaks marked with an asterisk are the strongest of multiplets related to the assigned formulation by addition or loss of one or two H atoms.

Starting Materials. Literature methods were used to prepare $W(C_2Ph)(CO)_3(\eta\text{-}C_5H_5)$,[14] $Mn(C_2Ph)(CO)_3(dppe)$,[15] $Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$,[14] $Ni(C_2Ph)(PPh_3)(\eta\text{-}C_5H_5)$,[14] and $C(CN)_2{=}C(CF_3)_2$ (dcfe).[5] $Me_3NO{\cdot}2H_2O$ (Aldrich) was used as received.

Reactions of $C(CN)_2{=}C(CF_3)_2$. (a) With $W(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$. To a solution of $W(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$ (250 mg, 0.57 mmol) in dichloromethane (30 mL) was added dcfe (160 mg, 0.75 mmol). After the mixture was stirred in the dark for 45 min, the volume was reduced under vacuum to 5 mL and a mixture of EtOH (2 mL) and petroleum spirit (5 mL) was added. Further reduction in volume and cooling resulted in a yellow precipitate. The solution was syringed off and the precipitate washed with petroleum spirit and dried under vacuum. Thin-layer chromatography (TLC) (silica) of the product (2.5:1 petroleum spirit/acetone) separated a major yellow band (R_f 0.55) from four yellow/orange trace bands. Crystallization of the major product (dichloromethane/petroleum spirit) yielded yellow crystals of $W\{C{=}CPhC(CF_3)_2C(CN)_2\}(CO)_3(\eta\text{-}C_5H_5)$ (**6**) (330 mg, 0.49 mmol, 86%), mp 157–158 °C. Anal. Calcd for $C_{22}H_{10}F_6N_2O_3W$: C, 40.8; H, 1.6; N, 4.3; M_r, 648. Found: C, 40.7; H, 1.6; N, 4.3; M_r (mass spectrometry), 648. FAB mass spectrum: 648, $[M]^+$, 74; 620*, $[M - CO]^+$, 8; 592, $[M - 2CO]^+$, 100; 579*, $[M - CF_3]^+$, 9; 564, $[M - 3CO]^+$, 68; 495, $[M - 3CO - CF_3]^+$, 31; 406, $[WC_2PhC_2(CN)(CF_3) + 2H]^+$, 14; 368*, $[W_2]^+$?, 22; 350, $[M - 3CO - dcfe]^+$, 29; 305, $[W(CO)_2(C_5H_5)]^+$, 40; 287, $[H_2W(C_2Ph)]^+$?, 67. Aggregate ions above m/z 648 were observed at m/z 688 (6), 702 (14), 717 (18), 732 (8), 1128 (8), 1142 (2), and 1156 (2%).

(b) With $Mn(C_2Ph)(CO)_3(dppe)$. The olfein (80 mg, 0.37 mmol) was added to a solution of $Mn(C_2Ph)(CO)_3(dppe)$ (200 mg, 0.31 mmol) in benzene (20 mL). After the solution was stirred for 18 h, the white precipitate was filtered off and washed with benzene and petroleum spirit. Crystallization from dichloromethane/ethanol formed white crystals of $Mn\{C{=}CPhC(CF_3)_2C(CN)_2\}(CO)_3(dppe)$ (**7**) (200 mg, 0.23 mmol, 75%), mp 193–195 °C. Anal. Calcd for $C_{43}H_{29}F_6MnN_2O_3P_2$: C, 60.6; H, 3.4; N, 3.3; M_r 852. Found: C, 60.4; H, 3.5; N, 3.3; M_r (mass spectrometry), 852. FAB mass spectrum: 853, $[M + H]^+$, 4; 852, $[M]^+$, 4; 797*, $[M + H - 2CO]^+$, 2; 768, $[M - 3CO]^+$, 50; 742, $[M - 3CO - CN]^+$, 4; 691, $[M - 3CO - Ph]^+$, 5; 554, $[M - 3CO - dcfe]^+$, 8; 537, $[Mn(CO)_3(dppe)]^+$, 5; 479, $[Mn(CN)(dppe)]^+$, 8; 472, $[MnF(dppe)]^+$, 100; 453, $[Mn(dppe)]^+$, 15; 321, $[dppe - Ph]^+$, 28; 292, $[P_2Ph_3 - H]^+$, 17; 289, $[C_2PhC_2(CN)(CF_3)_2]^+$, 13; 276, $[Ph_3PO - 2H]^+$, 11; 259 $[MnF(PPh_2)]^+$, 16; 185, $[PPh_2]^+$, 74; 183, $[C_{12}H_8P]^+$, 56. Weak ions (<2%) were also found at m/z 1008, 1138, 1221, and 1406.

(c) With $Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$. Addition of dcfe (260 mg, 1.20 mmol) to a solution of $Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.72 mmol) in diethyl ether (30 mL) followed by stirring in the dark for 40 min resulted in a yellow solution. Reduction of the volume (5 mL) followed by filtration removed a small amount of unidentified precipitate (8 mg) which was washed with petroleum spirit (10 mL). The volume of the combined filtrates was then reduced until a yellow precipitate formed. After cooling, the pale solution was syringed off and the precipitate washed with petroleum spirit. Crystallization (dichloromethane/petroleum spirit) gave pale yellow crystals of $Fe\{C{=}CPhC(CF_3)_2C(CN)_2\}(CO)_2(\eta\text{-}C_5H_5)$ (**8**) (350 mg, 0.71 mmol, 98%), mp 96–97 °C. Anal. Calcd for $C_{21}H_{10}F_6FeN_2O_2$: C, 51.3; H, 2.1; N, 5.7; M_r, 492. Found: C, 50.5; H, 2.1; N, 5.9; M_r (mass spectrometry), 492. Rapid decomposition of the solid sample precluded more accurate analytical figures being obtained. FAB mass spectrum: 493, $[M + H]^+$, 18; 492, $[M]^+$, 11; 466, $[M - CN]^+$, 7; 436, $[M - 2CO]^+$, 100; 417, [M

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$- 2CO - F]^+$, 21; 410, $[M - 2CO - CN]^+$, 23; 398, $[M - 2CO - 2F]^+$, 7; 367, $[M - 2CO - CF_3]^+$, 8; 297, $[C_2Ph(dcfe) - F + H]^+$, 17; 277, $[M - H - dcfe]^+$, 37; 270, $[C_2PhC_2(CN)(CF_3)_2 - F]^+$, 45; 222, $[Fe(C_2Ph)(C_5H_5)]^+$, 6; 186, $[Fe(C_5H_5)_2]^+$, 27; 177, $[Fe(CO)_2(C_5H_5)]^+$, 17. The spectrum also contained many ions between *m/z* 500 and *m/z* 1420 with relative intensities <2%, except for those at *m/z* 557, 613, 872, and 918, which had relative intensities 10–15%.

(d) With $Ni(C_2Ph)(PPh_3)(\eta\text{-}C_5H_5)$. A mixture of $Ni(C_2Ph)(PPh_3)(\eta\text{-}C_5H_5)$ (200 mg, 0.41 mmol) and dcfe (140 mg, 0.65 mmol) was refluxed in benzene (50 mL) for 24 h. The solution was cooled, filtered, and evaporated to dryness. Two crystallizations from dichloromethane/ethanol followed by slow recrystallization from dichloromethane/petroleum spirit gave yellow-green crystalline $Ni\{C[{=}C(CN)_2]CPh{=}C(CF_3)_2\}(PPh_3)(\eta\text{-}C_5H_5)\cdot 0.25CH_2Cl_2$ (**11**), mp 156–157 °C. Anal. Calcd for $C_{37}H_{25}F_6N_2NiP\cdot 0.25CH_2Cl_2$: C, 61.9; H, 3.6; N, 3.9; M_r (unsolvated), 700. Found: C, 61.7; H, 3.5; N, 3.9; M_r (mass spectrometry), 700. FAB mass spectrum: 700 $[M]^+$, 31; 635, $[M - C_5H_5]^+$, 5; 582, $[M + H - C_2F_5]^+$, 17; 385, $[Ni(PPh_3)(C_5H_5)]^+$, 100; 320, $[Ni(PPh_3)]^+$, 77; 241*, $[Ni(PPh_2) - 2H]^+$, 67.

Conversion of 6 to Butadienyl 9 and Allyl 10. A solution of complex **6** (130 mg, 0.20 mmol) in xylene (50 mL) was refluxed for 2.45 h. After cooling, solvent was removed under vacuum and the residue chromatographed by TLC (2:1 petroleum spirit/acetone) which eluted two major yellow bands and three minor bands (uncharacterized). The first yellow band (R_f 0.60) was crystallized (dichloromethane/petroleum spirit) to give yellow crystalline $W\{C[{=}C(CN)_2]CPh{=}C(CF_3)_2\}(CO)_3(\eta\text{-}C_5H_5)$ (**9**) (11 mg, 0.02 mmol, 8%), mp 184–185 °C. Anal. Calcd for $C_{22}H_{10}F_6N_2O_3W$: C, 40.77; H, 1.56; N, 4.32; M_r, 648. Found: C, 40.56; H, 1.53; N, 4.29; M_r (mass spectrometry), 648. FAB mass spectrum: 648, $[M]^+$, 58; 620, $[M - CO]^+$, 75; 593, $[M + H - 2CO]^+$, 33; 564, $[M - 3CO]^+$, 100; 545*, $[M - 3CO - F]^+$, 38; 517*, $[W_2F(C_2H_5)_2]^+$, 17; 497*, $[M - 3CO - CF_3 + 2H]^+$, 9; 452*, $[W_2F(C_5H_5)]^+$, 8; 314*, $[W(C_5H_5)_2]^+$, 24.

The second yellow band (R_f 0.50) was crystallized (dichloromethane/MeOH) to give orange crystalline $W\{\eta^3\text{-}C(CN)_2CPhC{=}C(CF_3)_2](CO)_2(\eta\text{-}C_5H_5)$ (**10**) (32 mg, 0.05 mmol, 26%), mp 230–234 °C. Anal. Calcd for $C_{21}H_{10}F_6N_2O_2W$: C, 40.67; H, 1.63; N, 4.52; M_r, 620. Found: C, 40.57; H, 1.63; N, 4.50; M_r (mass spectrometry), 620. FAB mass spectrum: 620*, $[M]^+ + [M + H]^+$, 100; 564*, $[M - 2CO]$, 71; 545*, $[M - 2CO - F]^+$, 57.

Hydrolysis of 6. To a solution of complex **6** (150 mg, 0.23 mmol) in acetone (20 mL) was added $Me_3NO\cdot 2H_2O$ (8.5 mg, 0.84 mmol). After 1.5 h of stirring in the dark, the solvent was removed under vacuum. The orange residue was chromatographed by TLC (2:1:1 petroleum spirit/acetone/dichloromethane) when the product separated as a major orange band (R_f 0.50) from six trace bands. Crystallization of the orange band (dichloromethane/petroleum spirit) gave orange crystalline $W\{NH{=}C(OH)C(CN){=}CCPh{=}C(CF_3)_2\}(CO)_2(\eta\text{-}C_5H_5)\cdot 0.25CH_2Cl_2$ (**12**) (35 mg, 0.055 mmol, 24%), mp 222 °C dec. Anal. Calcd for $C_{21}H_{12}F_6N_2O_3W\cdot 0.25CH_2Cl_2$: C, 38.7; H, 1.9; N, 4.3; M_r (unsolvated), 638. Found: C, 38.3; H, 1.9; N, 4.3; M_r (mass spectrometry), 638. FAB mass spectrum: 638, $[M]^+$, 100; 613*, $[M - CO]^+$, 7; 598, $[M - 2HF]^+$, 14; 583, $[M + H - 2CO]^+$, 37; 562, $[M + H - Ph]^+$, 93; 517, $[M - 2CO - C_5H_5]^+$, 83; 284*, $[W(C_2Ph) - H]^+$, 49. Peaks at higher mass were found at *m/z* (relative intensity) 661 (14), 719 (10), 734 (5), and 748 (4%).

Single-Crystal X-ray Diffraction Studies of 6–8 and 12. Intensity data for **6**–**8** and **12** were measured at room temperature on an Enraf-Nonius CAD4F diffractometer fitted with Mo $K\bar{\alpha}$ (graphite monochromator) radiation, $\lambda = 0.71073$ Å, with the use of the $\omega/2\theta$ scan technique. No significant decomposition of any of the samples occurred during their respective data collections. The intensity data sets were corrected for Lorentz and polarization effects,[16] and for **6**–**8** analytical absorption corrections were also applied.[17] Relevant crystal data are given in Table VIII.

The structures were solved by Patterson methods, and each was refined by a full-matrix least-squares procedure in which the function $\sum w\Delta^2$ was minimized,[17] where $\Delta = ||F_o| - |F_c||$ and w was the weight applied to each reflection. For **6** only the tungsten atom was refined with anisotropic thermal parameters whereas the non-phenyl, non-hydrogen atoms in the remaining structures were refined anisotropically. Phenyl rings were refined as hexagonal rigid groups in each structure. Hydrogen atoms were included in the models for **7** and **8** at their calculated positions but were not included for the tungsten structures. The analysis of variance for **8** indicated no special features, and hence a weighting scheme was not applied. A weighting scheme of the form $w = k/[\sigma^2(F) + g|F|^2]$ was included for **6**, **7**, and **12**, and the refinement continued until convergence in each case. Differences in the Friedel pairs included in the data set for **6** enabled assignment of the absolute configuration of the structure with the use of Hamilton's significance test;[19] however, the limited accuracy of the analysis is noted. It was not possible to assign the absolute configuration of **7** on the basis of differences in measured Friedel pairs. Final refinement details are listed in Table VIII.

Scattering factors for the atoms C, H, F, N, O, and P were those incorporated in SHELX while those for the neutral metal atoms (Mn, Fe, W) were from ref 18 (the values being corrected for $\Delta f'$ and $\Delta f''$). The diagrams, shown in Figures 1–4, were drawn with ORTEP.[20]

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Registry No. **6**, 111112-34-6; **7**, 111159-35-4; **8**, 111112-35-7; **9**, 111112-38-0; **10**, 111139-78-7; **11**, 111139-77-6; **12**, 111112-36-8; $C(CN)_2{=}C(CF_3)_2$, 1113-69-5; $W(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$, 111112-37-9; $Mn(C_2Ph)(CO)_3(dppe)$, 93442-19-4; $Fe(C_2Ph)(CO)_2(\eta\text{-}C_5H_5)$, 12308-30-4; $Ni(C_2Ph)(PPh_3)(\eta\text{-}C_5H_5$, 1299-04-3; Me_3NO, 1184-78-7.

Supplementary Material Available: Tables of anisotropic thermal parameters for **6**–**8** and **12**, tables of bond distances and angles for **6**–**8**, and tables of hydrogen atom parameters for **7** and **8** (13 pages); listings of observed and calculated structure factors for **6**–**8** and **12** (62 pages). Ordering information is given on any current masthead page.

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