Allylic Alkylation of Co-ordinated Cyanide; the Synthesis and X-Ray Crystal Structure of *trans*-$[Mn(CO)(CNCH_2CMe = CH_2)(dppm)_2][PF_6]\cdot thf$* (dppm = $Ph_2PCH_2PPh_2$, thf = tetrahydrofuran)

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The reaction of *trans*-$[Mn(CN)(CO)(dppm)_2]$ with $[Fe\{P(OMe)_3\}(NO)_2(\eta\text{-}C_3H_4R)][PF_6]$ (R = H, 1-Me, or 2-Me) in tetrahydrofuran (thf) results in allylic alkylation of the cyanide ligand to give the allyl isocyanide complexes *trans*-$[Mn(CO)(CNCH_2CMe{=}CH_2)(dppm)_2][PF_6]\cdot thf$ and *trans*-$[Mn(CO)(CNCH_2CH{=}CHR)(dppm)_2][PF_6]\cdot thf$ (R = H or Me). The X-ray crystal structure of *trans*-$[Mn(CO)(CNCH_2CMe{=}CH_2)(dppm)_2][PF_6]\cdot thf$ shows that in the cation the manganese(I) atom has approximately octahedral co-ordination, with the carbonyl and 2-methylallyl isocyanide ligands mutually *trans*, and the chelating dppm ligands occupying the four equatorial sites.

The complexes $[Fe\{P(OMe)_3\}(NO)_2(\eta\text{-}C_3H_4R)][PF_6]$ (R = H, 1-Me, or 2-Me) are stable and convenient sources of the electrophilic allyl cations $[C_3H_4R]^+$, their reactions with $[ML_n(\eta^4\text{-cot})]$ (cot = cyclooctatetraene) resulting in allylic alkylation of either the cot [ML_n = $Fe(CO)_2(CNBu^t)$, $Ru(CO)_3$,[1] $Co(\eta\text{-}C_5R_5)$ (R = H or Me)[2]] or the cyclopentadienyl [ML_n = $Rh(\eta\text{-}C_5H_5)$][3] rings. We now show that the reaction of $[Fe\{P(OMe)_3\}(NO)_2(\eta\text{-}C_3H_4R)][PF_6]$ with *trans*-$[Mn(CN)(CO)(dppm)_2]$(dppm = $Ph_2PCH_2PPh_2$) leads to cyanide alkylation, an X-ray crystal structural analysis of *trans*-$[Mn(CO)(CNCH_2CMe{=}CH_2)(dppm)_2][PF_6]\cdot thf$ (thf = tetrahydrofuran) reveal the formation of co-ordinated allyl isocyanide.

Results and Discussion

The treatment of a tetrahydrofuran solution of *trans*-$[Mn(CN)(CO)(dppm)_2]$ with solid $[Fe\{P(OMe)_3\}(NO)_2(\eta\text{-}C_3H_4R)][PF_6]$ (R = H, 1-Me, or 2-Me) results in the formation of brown solutions from which the orange salts *trans*-$[Mn(CO)(CNCH_2CMe{=}CH_2)(dppm)_2][PF_6]\cdot thf$ and *trans*-$[Mn(CO)(CNCH_2CH{=}CHR)(dppm)_2][PF_6]\cdot thf$ (R = H or Me) can be isolated as crystalline thf solvates after chromatography on alumina. The complexes were characterised (Experimental section) by elemental analysis {difficulty was found in acquiring satisfactory data for *trans*-$[Mn(CO)(CNCH_2CH{=}CH_2)(dppm)_2][PF_6]\cdot thf$} and by NMR and IR spectroscopy.

The ^1H NMR spectra of *trans*-$[Mn(CO)(CNCH_2CH{=}CHR)(dppm)_2][PF_6]\cdot thf$ (R = H or Me) were largely uninformative with resonances due to the $CH_2CH{=}CHR$ moieties obscured by those of the dppm ligands and the thf of solvation. {The observation of only one doublet (J 6.6 Hz) for the Me group does suggest that only one isomer is formed using $[Fe\{P(OMe)_3\}(NO)_2(\eta\text{-}C_3H_4Me\text{-}1)][PF_6]$; the chemical shift ($\delta$ 0.63) indicates the presence of *trans*-$[Mn(CO)(CNCH_2CH{=}CHMe)(dppm)_2][PF_6]\cdot thf$ rather than $[Mn(CO)(CNCHMeCH{=}CH_2)(dppm)_2][PF_6]$, *i.e.* that allylic alkylation is selective at the less-substituted terminal carbon atom}. However, the spectrum of *trans*-$[Mn(CO)(CNCH_2CMe{=}CH_2)(dppm)_2][PF_6]\cdot thf$ was in full agreement with the presence of the allyl isocyanide ligand. In addition, the overall *trans* geometry of the complexes was confirmed by the ^{31}P NMR spectrum of $[Mn(CO)(CNCH_2CH{=}CH_2)(dppm)_2][PF_6]\cdot thf$ which showed one singlet resonance at δ 39.99 (apart from the septet due to the $[PF_6]^-$ ion), *i.e.* that the two dppm ligands are equivalent.

The IR spectrum of each of the compounds showed one carbonyl band and one cyanide band both shifted to higher energy than those of *trans*-$[Mn(CN)(CO)(dppm)_2]$ [$\nu(CO)$ 1865, $\nu(CN)$ 2085 cm^{-1}]. These bands are similar in energy to those of the cationic complex *trans*-$[Mn(CNMe)(CO)(dppm)_2]^+$ [$\nu(CO)$ 1903, $\nu(CN)$ 2151 cm^{-1}]; further evidence for isocyanide ligand formation is provided by the increase in the intensity of the cyanide absorption and by the observation of a reversible one-electron oxidation wave at 0.55 V in the cyclic voltammogram in CH_2Cl_2 {*cf.* 0.51 and 0.07 V for *trans*-$[Mn(CNMe)(CO)(dppm)_2]^+$ and *trans*-$[Mn(CN)(CO)(dppm)_2]$ respectively}.[4] However, definitive proof of the allylic alkylation of the co-ordinated cyanide ligand was provided by an X-ray structural study of $[Mn(CO)(CNCH_2CMe{=}CH_2)(dppm)_2][PF_6]\cdot thf$.

Table 1 lists selected bond lengths and interbond angles derived from the structure analysis, and Fig. 1 shows the molecular structure of the cation. The crystal structure consists of isolated molecular ions and solvent molecules, with the shortest intermolecular contacts involving O(1) $\cdots$ H(29A) 2.39 Å (the carbonyl oxygen and a probably disordered phenyl group hydrogen) and F(2) $\cdots$ H(3A) 2.50 Å (a $[PF_6]^-$ fluorine and a $CNCH_2$ hydrogen). Within the cation, the manganese(I) atom has approximately octahedral co-ordination, with the carbonyl and 2-methylallyl isocyanide ligands mutually *trans*, and the chelating dppm ligands occupying the four equatorial sites. The Mn–CN [1.929(9) Å] and Mn–CO [1.784(9) Å] distances fall within typical ranges.[5] The largest deviations from ideal octahedral angles at Mn are, of course, associated with the restricted bite of the chelating dppm ligands [P(1)–Mn–P(2)

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* *trans*-Bis[bis(diphenylphosphino)methane-κ*P*,*P*′]carbonyl(2-methylallyl isocyanide-κ*C*)manganese hexafluorophosphate–tetrahydrofuran(1/1).

Supplementary data available: See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Selected bond lengths (Å) and interbond angles (°) for *trans*-$[Mn(CO)(CNCH_2CMe{=}CH_2)(dppm)_2][PF_6]\cdot thf$

Mn–P(1)	2.289(3)	P(5)–F(4)	1.505(14)	C(20)–C(21)	1.417(14)	C(40)–C(41)	1.385(16)
Mn–P(2)	2.289(3)	P(5)–F(5)	1.508(12)	C(20)–C(25)	1.334(14)	C(41)–C(42)	1.326(16)
Mn–P(3)	2.319(3)	P(5)–F(6)	1.498(13)	C(21)–C(22)	1.381(17)	C(42)–C(43)	1.407(14)
Mn–P(4)	2.295(3)	N(1)–C(2)	1.132(11)	C(22)–C(23)	1.321(18)	C(45)–C(46)	1.353(13)
Mn–C(1)	1.784(9)	N(1)–C(3)	1.431(12)	C(23)–C(24)	1.388(18)	C(45)–C(50)	1.419(13)
Mn–C(2)	1.929(9)	O(1)–C(1)	1.161(12)	C(24)–C(25)	1.400(17)	C(46)–C(47)	1.401(16)
P(1)–C(19)	1.844(9)	C(3)–C(4)	1.515(13)	C(26)–C(27)	1.374(16)	C(47)–C(48)	1.348(16)
P(1)–C(20)	1.832(10)	C(4)–C(5)	1.466(16)	C(26)–C(31)	1.365(15)	C(48)–C(49)	1.387(16)
P(1)–C(26)	1.834(10)	C(4)–C(6)	1.290(19)	C(27)–C(28)	1.444(17)	C(49)–C(50)	1.403(17)
P(2)–C(7)	1.832(9)	C(7)–C(8)	1.353(14)	C(28)–C(29)	1.318(19)	C(51)–C(52)	1.401(16)
P(2)–C(13)	1.823(10)	C(7)–C(12)	1.394(14)	C(29)–C(30)	1.285(20)	C(51)–C(56)	1.376(14)
P(2)–C(19)	1.857(10)	C(8)–C(9)	1.418(14)	C(30)–C(31)	1.467(17)	C(52)–C(53)	1.444(20)
P(3)–C(44)	1.829(9)	C(9)–C(10)	1.388(16)	C(32)–C(33)	1.392(14)	C(53)–C(54)	1.392(22)
P(3)–C(45)	1.817(9)	C(10)–C(11)	1.374(18)	C(32)–C(37)	1.357(15)	C(54)–C(55)	1.366(21)
P(3)–C(51)	1.831(10)	C(11)–C(12)	1.437(16)	C(33)–C(34)	1.370(18)	C(55)–C(56)	1.423(17)
P(4)–C(32)	1.816(10)	C(13)–C(14)	1.371(14)	C(34)–C(35)	1.385(18)	C(57)–C(59)	1.588(50)
P(4)–C(38)	1.828(9)	C(13)–C(18)	1.387(15)	C(35)–C(36)	1.370(19)	C(57)–C(61)	1.732(49)
P(4)–C(44)	1.856(10)	C(14)–C(15)	1.432(15)	C(36)–C(37)	1.414(19)	C(58)–C(60)	1.279(67)
P(5)–F((1)	1.556(9)	C(15)–C(16)	1.351(16)	C(38)–C(39)	1.379(14)	C(58)–C(61)	1.234(60)
P(5)–F(2)	1.564(11)	C(16)–C(17)	1.344(18)	C(38)–C(43)	1.397(14)	C(59)–C(60)	1.639(60)
P(5)–F(3)	1.553(10)	C(17)–C(18)	1.427(17)	C(39)–C(40)	1.418(14)		

P(1)–Mn–P(2)	72.9(1)	P(3)–Mn–C(2)	86.3(3)	Mn–P(2)–C(19)	94.9(3)	Mn–P(4)–C(44)	94.5(3)
P(1)–Mn–P(3)	176.8(1)	P(4)–Mn–C(2)	87.9(3)	C(7)–P(2)–C(19)	105.6(4)	C(32)–P(4)–C(44)	105.4(4)
P(2)–Mn–P(3)	106.8(1)	C(1)–Mn–C(2)	176.9(4)	C(13)–P(2)–C(19)	105.3(4)	C(38)–P(4)–C(44)	105.5(4)
P(1)–Mn–P(4)	107.8(1)	Mn–P(1)–C(19)	95.2(3)	Mn–P(3)–C(44)	94.4(3)	C(2)–N(1)–C(3)	178.5(9)
P(2)–Mn–P(4)	179.0(1)	Mn–P(1)–C(20)	125.2(3)	Mn–P(3)–C(45)	123.5(3)	Mn–C(1)–O(1)	176.3(8)
P(3)–Mn–P(4)	72.5(1)	C(19)–P(1)–C(20)	105.4(4)	C(44)–P(3)–C(45)	107.1(4)	Mn–C(2)–N(1)	177.3(8)
P(1)–Mn–C(1)	87.0(3)	Mn–P(1)–C(26)	122.1(3)	Mn–P(3)–C(51)	124.2(3)	N(1)–C(3)–C(4)	111.0(8)
P(2)–Mn–C(1)	88.3(3)	C(19)–P(1)–C(26)	105.2(4)	C(44)–P(3)–C(51)	103.1(4)	C(3)–C(4)–C(5)	115.7(9)
P(3)–Mn–C(1)	96.2(3)	C(20)–P(1)–C(26)	100.8(4)	C(45)–P(3)–C(51)	101.1(4)	C(3)–C(4)–C(6)	118.8(11)
P(4)–Mn–C(1)	91.1(3)	Mn–P(2)–C(7)	123.8(3)	Mn–P(4)–C(32)	118.2(3)	C(5)–C(4)–C(6)	125.5(11)
P(1)–Mn–C(2)	90.5(3)	Mn–P(2)–C(13)	123.0(3)	Mn–P(4)–C(38)	126.4(3)		
P(2)–Mn–C(2)	92.8(3)	C(7)–P(2)–C(13)	101.3(4)	C(32)–P(4)–C(38)	103.7(4)		

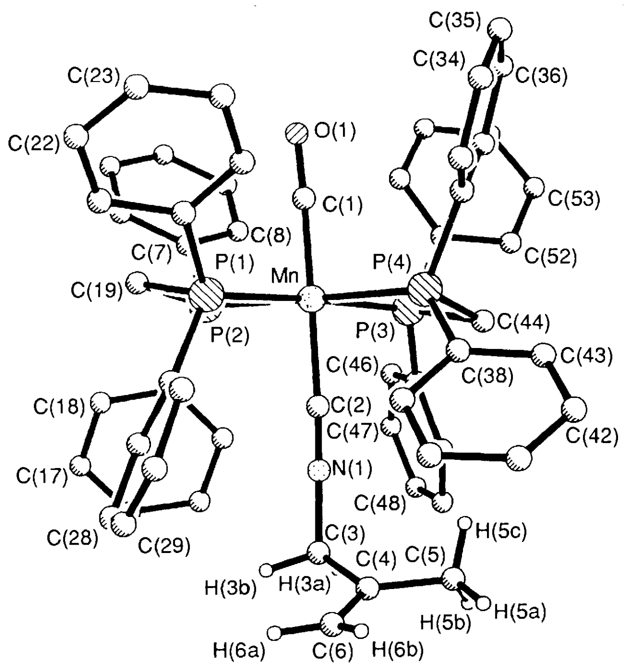

Fig. 1 The molecular structure of the cation *trans*-$[Mn(CO)(CNCH_2CMe{=}CH_2)(dppm)_2]^+$ showing the atom labelling scheme

72.9(1), P(3)–Mn–P(4) 72.5(1), P(1)–Mn–P(4) 107.8(1), and P(2)–Mn–P(3) 106.8(1)°]. The chelate rings of the two dppm ligands are folded about the P... P vectors (by 16 and 18° respectively) in such a way that the CH_2 groups are on opposite sides of the MnP_4 plane. The 2-methylallyl isocyanide ligand is near-linear at C(2) and N(1) and has an orthodox geometry.

Electrophilic attack on manganese-co-ordinated cyanide has previously been observed. For example, protonation of *trans*-$[Mn(CN)(CO)_2\{P(OPh)_3\}(dppm)]^+$ gives *trans*-$[Mn(CNH)(CO)_2\{P(OPh_3\}(dppm)]^{2+}$,[6] and *cis*- or *trans*-$[Mn(CN)(CO)_2\{P(OPh)_3\}(dppm)]$ reacts with MeI to give *cis*- or *trans*-$[Mn(CNMe)(CO)_2\{P(OPh)_3\}(dppm)]^+$.[7] However, the formation of allyl isocyanides by electrophilic addition to CN is unprecedented.

The mechanism of the allyl-transfer reaction from iron to the cyanide N atom most likely involves the formation of a bimetallic intermediate (as in the allylic alkylation of co-ordinated cot ligands). An IR spectrum taken shortly after mixing *trans*-$[Mn(CN)(CO)(dppm)_2]$ and $[Fe\{P(OMe)_3\}(NO)_2(\eta\text{-}C_3H_5)]$ [ν(NO) 1845 and 1791 cm^{-1}] showed new nitrosyl bands at 1758 and 1710 cm^{-1} which may be assigned to an unstable intermediate in which the allyl group is σ bound to the cyanide N atom and η^2 bound to iron; cleavage of the alkene–iron linkage eventually leads to the other observed product of the reactions, namely $[Fe\{P(OMe)_3\}_2(NO)_2]$ [ν(NO) 1739 and 1686 cm^{-1} (CH_2Cl_2)].

Experimental

The preparation and purification of the complexes described were carried out under an atmosphere of dry nitrogen, using dried, distilled, and deoxygenated solvents. The reactions were carried out in flasks shielded from light by aluminium foil; the progress of a reaction was monitored by IR spectroscopy.

The complexes *trans*-$[Mn(CN)(CO)(dppm)_2]$[8] and $[Fe\{P(OMe)_3\}(NO)_2(\eta\text{-}C_3H_4R)][PF_6]$ (R = H, 1-Me, or 2-Me)[9] were prepared by published methods.

Electrochemical studies were carried out as previously described[4] using an E.G. and G. Par 273 potentiostat. Under the conditions used E° for the couple $[Fe(\eta\text{-}C_5Me_5)_2]^+$-$[Fe(\eta\text{-}C_5Me_5)_2]$, used as an internal standard, is −0.09 V. Infrared spectra were recorded on a Nicolet 5ZDX FT spectrometer; ^1H

Table 2 Atomic coordinates (× 10^4) for *trans*-[Mn(CO)(CNCH$_2$CMe=CH$_2$)(dppm)$_2$][PF$_6$]·thf

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mn	13(1)	1701(1)	2241(1)	C(25)	−2521(9)	2668(5)	2711(5)
P(1)	−429(2)	2588(1)	2129(1)	C(26)	−508(9)	2927(4)	1326(5)
P(2)	1687(2)	2165(1)	2573(1)	C(27)	486(11)	3013(5)	1013(6)
P(3)	499(2)	803(1)	2297(1)	C(28)	414(13)	3271(5)	375(7)
P(4)	−1658(2)	1225(1)	1923(1)	C(29)	−658(12)	3383(5)	118(7)
P(5)	2923(3)	787(1)	8643(2)	C(30)	−1643(12)	3319(5)	362(6)
N(1)	629(7)	1667(3)	808(3)	C(31)	−1574(10)	3070(5)	1018(6)
O(1)	−676(7)	1813(3)	3594(3)	C(32)	−2692(8)	1109(4)	2532(5)
F(1)	3037(9)	342(3)	8119(4)	C(33)	−3748(9)	1387(4)	2490(6)
F(2)	2844(10)	1202(3)	9212(6)	C(34)	−4464(12)	1356(5)	2992(6)
F(3)	2136(9)	405(3)	9009(5)	C(35)	−4148(12)	1054(5)	3552(7)
F(4)	3603(13)	1176(4)	8265(7)	C(36)	−3121(12)	771(6)	3591(7)
F(5)	3973(9)	548(6)	9041(7)	C(37)	−2390(11)	800(5)	3069(6)
F(6)	1854(10)	1011(6)	8257(7)	C(38)	−2592(8)	1300(4)	1147(5)
C(1)	−387(8)	1753(4)	3066(5)	C(39)	−2487(9)	1737(4)	746(5)
C(2)	378(7)	1671(3)	1334(4)	C(40)	−3203(9)	1786(5)	139(5)
C(3)	972(9)	1670(4)	149(5)	C(41)	−3948(10)	1366(5)	−47(6)
C(4)	−74(9)	1577(4)	−353(5)	C(42)	−4041(10)	936(5)	325(5)
C(5)	−552(11)	1034(5)	−375(6)	C(43)	−3355(9)	886(4)	934(5)
C(6)	−486(13)	1972(7)	−709(8)	C(44)	878(8)	582(4)	1850(5)
C(7)	2496(8)	2095(4)	3391(4)	C(45)	1681(8)	512(3)	1880(4)
C(8)	2756(8)	1602(4)	3631(5)	C(46)	2752(9)	437(4)	2208(5)
C(9)	3338(9)	1525(5)	4273(5)	C(47)	3713(11)	258(5)	1891(6)
C(10)	3654(10)	1973(5)	4650(6)	C(48)	3573(11)	149(5)	1239(6)
C(11)	3427(10)	2481(5)	4417(6)	C(49)	2494(10)	214(5)	876(6)
C(12)	2817(9)	2544(5)	3771(5)	C(50)	1543(9)	408(4)	1191(5)
C(13)	2880(8)	2253(4)	2050(4)	C(51)	584(9)	405(4)	3056(5)
C(14)	3138(8)	1845(4)	1640(5)	C(52)	436(10)	−147(5)	2987(6)
C(15)	4070(9)	1898(5)	1222(5)	C(53)	510(13)	−461(7)	3585(7)
C(16)	4670(10)	2363(5)	1245(6)	C(54)	771(12)	−215(6)	4196(8)
C(17)	4456(11)	2767(5)	1651(6)	C(55)	901(11)	324(6)	4257(7)
C(18)	3515(9)	2724(5)	2060(5)	C(56)	785(9)	638(5)	3670(5)
C(19)	948(8)	2823(4)	2580(5)	C(57)	4538(30)	609(12)	6637(16)
C(20)	−1602(8)	2930(4)	2514(4)	C(58)	4613(40)	769(14)	5609(19)
C(21)	−1493(9)	3488(4)	2612(5)	C(59)	5746(30)	496(13)	6340(19)
C(22)	−2377(11)	3763(5)	2881(6)	C(60)	5674(43)	636(18)	5549(23)
C(23)	−3298(11)	3498(5)	3052(6)	C(61)	3711(33)	733(14)	5893(20)
C(24)	−3401(11)	2948(5)	2996(6)				

and ^{31}P NMR spectra were recorded in [$^2H_6$]acetone on JEOL GX400 and FX 90Q spectrometers, and were calibrated against SiMe$_4$ as an internal reference and H$_3$PO$_4$ as an external reference respectively. Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

trans-Bis[*bis*(*diphenylphosphino*)*methane-κP,P′*]*-carbonyl*(*2-methylallyl isocyanide-κC*)*manganese Hexafluorophosphate–Tetrahydrofuran* (1:1), *trans*-[Mn(CO)(CNCH$_2$CMe=CH$_2$)(dppm)$_2$][PF$_6$]·thf.—To an orange solution of *trans*-[Mn(CN)(CO)(dppm)$_2$] (55 mg, 0.064 mmol) in thf (10 cm^3) was added [Fe{P(OMe)$_3$}(NO)$_2$(η-C$_3$H$_4$Me-2)][PF$_6$] (28 mg, 0.064 mmol). Hexane was then added to the brown solution to give an orange precipitate which was redissolved in thf and added to an alumina–hexane chromatography column. A gradual increase in the proportion of thf in the eluting solvent (hexane–thf) first gave unreacted *trans*-[Mn(CN)(CO)(dppm)$_2$] and then an orange band (100% thf) which was evaporated to dryness. Dissolution of the residue in thf, addition of hexane, and partial removal of the solvent *in vacuo* gave the product as orange crystals, yield 12 mg (18%) (Found: C, 62.7; H, 5.4; N, 1.2. $C_{60}H_{59}F_6MnNO_2P_5$ requires C, 62.7; H, 5.2; N, 1.2%). IR (CH$_2$Cl$_2$): ν(CO) 1904, ν(CN) 2124 cm^{-1}. ^{1}H NMR ([$^2H_6$]-acetone): δ 1.22 (3 H, s, Me), 1.78 (4 H, m, thf), 3.54 (2 H, br s, H^{3a},H^{3b}), 3.62 (4 H, m, thf) 4.51 (1 H, s, H^{6a} or H^{6b}), 4.76 (1 H, s, H^{6a} or H^{6b}), 5.10 (4 H, m, Ph$_2$PC*H*$_2$PPh$_2$), 7.25 (16 H, m, *o*-H of Ph), 7.38 (16 H, m, *m*-H of Ph), and 7.52 (8 H, m, *p*-H of Ph).

The complexes *trans*-[Mn(CO)(CNCH$_2$CH=CH$_2$)(dppm)$_2$][PF$_6$]·thf [59%; ν(CO) 1903, ν(CN) 2131 cm^{-1}] and *trans*-[Mn(CO)(CNCH$_2$CH=CHMe)(dppm)$_2$][PF$_6$]·thf, 59%. (Found: C, 62.3; H, 5.8; N, 1.4. $C_{60}H_{59}F_6MnNO_2P_5$ requires C, 62.7; H, 5.2; N, 1.2%), ν(CO) 1903, ν(CN) 2117 cm^{-1}, were prepared similarly. All of the complexes are soluble in polar solvents such as CH$_2$Cl$_2$, thf, and acetone to give yellow solutions which decompose in air. The solid complexes decompose only slowly when stored under nitrogen at 0 °C.

Crystal Structure Analysis of trans-[Mn(CO)(CNCH$_2$CMe=CH$_2$)(dppm)$_2$][PF$_6$]·thf.—*Crystal data* $C_{60}H_{59}F_6MnNO_2P_5$, $M = 1194.9$, monoclinic, space group $P2_1/c$, $a = 11.459(2)$, $b = 25.075(5)$, $c = 20.309(3)$ Å, $\beta = 95.50(1)°$, $U = 5809(2)$ Å^3, $Z = 4$, $D_c = 1.23$ g cm^{-3}, $\bar{\lambda} = 0.710\,69$ Å, $\mu = 4.1$ cm^{-1}, $F(000) = 2384$, $T = 295$K.

Diffraction measurements were made with a Nicolet four-circle P3m diffractometer using graphite monochromated X-radiation on a single crystal (approximate dimensions 0.5 × 0.4 × 0.5 mm) mounted in a thin-walled glass capillary under N$_2$. Cell dimensions were determined from the setting angle values of 44 centred reflections. A total of 11 820 diffracted intensities (including checks) were measured in a unique quadrant of reciprocal space for $4.0 < 2\theta < 50.0°$ by ω–2θ scans of 2θ width $2.0° + \Delta_{\alpha_1\alpha_2}$. Three check reflections (3 12 0, $1\ 1\ \bar{1}0$, $63\bar{5}$) remeasured after every 50 ordinary data showed no decay and *ca.* 3% variation over the period of data collection; an appropriate correction for the slow intensity variation was therefore applied. Of the 11 010 non-check intensity data collected, 10 208 unique observations remained after averaging of duplicate and equivalent measurements and deletion of systematic absences. Of these 4 514 with $I > 2\sigma(I)$ were retained for use in structure solution and refinement. An absorption correction was applied on the basis of 666 azimuthal scan data; maximum and minimum transmission coefficients were 0.812 and 0.727 respectively. Lorentz and polarisation corrections were applied. The structure was solved by heavy-atom (Patterson and Fourier difference) methods, and refined by full-matrix least squares against F. All non-hydrogen atoms, other than carbon and solvent oxygen atoms (which were refined with isotropic displacement parameters), were assigned freely refined anisotropic displacement parameters. It was not possible to assign the oxygen atom of the solvent thf molecule, whose geometry is clearly distorted by what is presumably disorder; all non-hydrogen atoms of the thf were modelled as carbon, and the hydrogen atoms were not included. All hydrogen atoms were assigned fixed isotropic displacement parameters. The hydrogen atoms H(6a) and H(6b) of the allyl isocyanide ligand were refined without positional constraints. All other hydrogen atoms were constrained to ideal geometries with C–H 0.96 Å. Refinement of the 377 least-squares variables converged smoothly to residual indices $R = 0.083$, $R' = 0.097$, $S = 2.49$.* Weights, w, were set equal to $[\sigma_c^2(F_o) + gF_o^2]^{-1}$. Here $\sigma_c^2(F_o)$ is the variance in F_o due to counting statistics and $g = 0.0005$ was chosen to minimise the variation in S as a function of F_o. Final difference electron-density maps showed no features outside the range +0.7 to −0.5 e Å^{-3} with the largest of these all associated with the carbon atoms C(26)–C(31) of one phenyl ring, presumably indicating a degree of disorder in this group. Table 2 reports the positional parameters for the non-hydrogen atoms.

All calculations were made with programs of the SHELXTL-PLUS[10] system as implemented on a Nicolet R3m/V structure determination system. Complex neutral-atom scattering factors were taken from ref. 11.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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* $R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$; $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$; where $\Delta = F_o - F_c$ and N_o, N_v are the numbers of observations and variables.