Electrophilically Promoted Cyanide Abstraction in Diiron Cyano(amino)alkylidene Complexes: Molecular Structure of $[Fe_2(CO)_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)\{\mu\text{-}C\overline{N(CH_2)_4C}H_2\}]$-$[(OC)_5WCNW(CO)_5]$†

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The reactions of the μ-cyano(amino)alkylidene complexes $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)(NR_2)\}]$ [cp = $\eta^5\text{-}C_5H_5$, $NR_2 = \overline{N(CH_2)_4C}H_2$ **1a** or NMe_2 **1b**] with $[W(CO)_5(thf)]$ (thf = tetrahydrofuran), $MeSO_3CF_3$ and HSO_3CF_3 electrophiles promotes μ-C–CN bond cleavage with formation of the corresponding $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)(\mu\text{-}CNR_2)]^+$ **3**. In the case of $[W(CO)_5(thf)]$ the unexpected salts $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)(\mu\text{-}CNR_2)][(OC)_5WCNW(CO)_5]$ have been prepared and characterized by the crystal structure of **3a** [$NR_2 = \overline{N(CH_2)_4C}H_2$]. The structure [monoclinic, space group $P2_1/n$, a = 11.196(3), b = 17.389(3), c = 17.938(3) Å, β = 95.19(2)°, Z = 4, R = 0.032] contains ordered cations and anions. Distances of interest are Fe–μ-C(N) 1.875(6), C–N 1.280(8) Å in the cation and W–C(N) 2.184(8), W–N(C) 2.187(7) and C–N 1.15(1) Å in the anion, where the cyanide ligand symmetrically bridges two $W(CO)_5$ units. Electrophilic addition to phosphorus in $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)(PEt_2)\}]$ **2** has been observed and the adduct $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)[PEt_2W(CO)_5]\}]$ **4** spectroscopically characterized. The different reactivity of **1** and **2** with electrophilic reagents is attributed to the strong tendency to C=N double-bond formation.

We recently succeeded in synthesising a variety of unprecedented diiron μ-amino- and μ-phosphino-alkylidene complexes of the type $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)(ER_2)\}]$ (cp = η-C_5H_5, E = N or P).[1] Owing to their novelty, we initiated a study of their chemistry by investigating the reactions with Lewis acids which were expected to give addition at the nitrile N or at the μ-C bonded heteroatom lone pairs. Our previous work in this field showed that the reaction of $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)(SMe)\}]$ with $[W(CO)_5(thf)]$ (thf = tetrahydrofuran) forms stepwise both the monoadduct $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C[CNW(CO)_5](SMe)\}]$ and the diadduct $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C[CNW(CO)_5][SMeW(CO)_5]\}]$.[2] On the other hand, the same thioalkylidene has been easily S-methylated with $MeOSO_2CF_3$ to give the sulfonium complex $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)(SMe_2)\}]^+$.[1a] The latter displays residual ability to react with a Lewis acid in the formation of the octahedral iron(II) complex $[Fe(OSO_2CF_3)_4\{Fe_2(CO)_2(cp)_2(\mu\text{-}CO)[\mu\text{-}C(CN)(SMe_2)]\}_2]$,[2] where the sulfonium cation is co-ordinated *via* the nitrile nitrogen to the Fe^{II}.

Herein we report on the reactions of the aminoalkylidene $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)(NR_2)\}]$ ($NR_2 = \overline{N(CH_2)_4C}H_2$ **1a** or NMe_2 **1b**) and the phosphinoalkylidene $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)(PEt_2)\}]$ **2** with $[W(CO)_5(thf)]$ which form $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)(\mu\text{-}CNR_2)][(OC)_5WCNW(CO)_5]$ **3a** and **3b** and $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)[PEt_2W(CO)_5]\}]$ **4**, respectively. The unexpected type **3** salts have been characterized by the molecular structure of **3a**, determined by an X-ray diffraction study. Finally the reactions with $MeSO_3CF_3$ and HSO_3CF_3 are also examined.

Results and Discussion

The reactions of the aminoalkylidenes **1a** and **1b** with an excess of $[W(CO)_5(thf)]$ result in the formation of derivatives **3a** and **3b** (Scheme 1). The nature of salts **3** has been ascertained by an X-ray diffraction study of **3a**. Their spectroscopic properties are the sum of those due to the cation and the anion respectively. The IR spectrum of **3a** (in CH_2Cl_2 solution) shows absorptions in the carbonyl stretching region at 2059w, 1936vs and 1875 (sh) cm^{-1} consistent with values reported for the anion $[W_2(CO)_{10}(CN)]^-$ prepared by treating $[W(CO)_6]$ with CN^- under photolysis.[3] Furthermore, the ν(CO) bands at 2029s, 1983 (sh) and 1845 (sh) cm^{-1} can be associated with the cation $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C\overline{N(CH_2)_4C}H_2\}]^+$ in agreement with values reported for analogues $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}CNR(R')\}]^+$ obtained by N-alkylation of the corresponding isocyanide $[Fe_2(CO)_3(cp)_2(CNR)]$ derivatives.[4] The IR spectra of **3a** and **3b** also exhibit two ν(CN) absorptions due to the μ-CNR_2 ligand in the cation (at 1572 cm^{-1}) and to the bridging CN in the anion (at 2123 cm^{-1} for **3a**) respectively. The latter compares very well with the band previously reported (2121 cm^{-1}).[3]

The ^{13}C NMR spectrum of complex **3a** (in CD_2Cl_2) shows resonances at δ 208.2 and 253.6 attributable to the Fe–CO and at δ 202.9, 201.1, 199.0 and 198.0 due to the W–CO. The latter exhibit satellite peaks due to coupling with ^{183}W (J_{WC} in the range of 151–125 Hz). Moreover, a low-field resonance is observed at δ 315.5 for the carbyne carbon and a signal at δ 153.4 attributable to the carbon of the bridging nitrile group. A single cp resonance occurs at δ 90.2 (at δ 5.16 in the ^1H NMR spectrum) suggesting that a single isomer, presumably that observed in the solid state, is present in solution.

Like $[W(CO)_5(thf)]$, both HSO_3CF_3 and $MeSO_3CF_3$ react with **1a** and **1b** to abstract the nitrile group with formation of the corresponding μ-aminocarbyne complexes $[Fe_2(CO)_2$-

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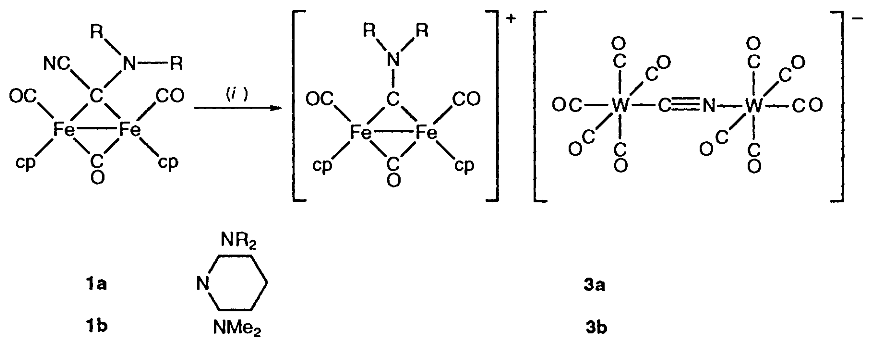
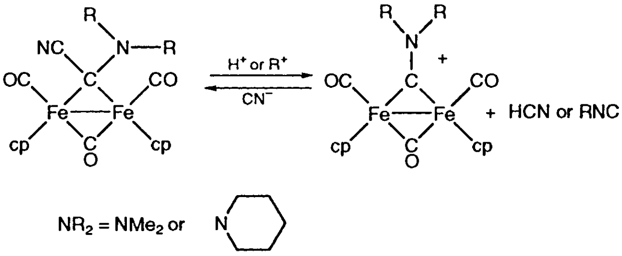
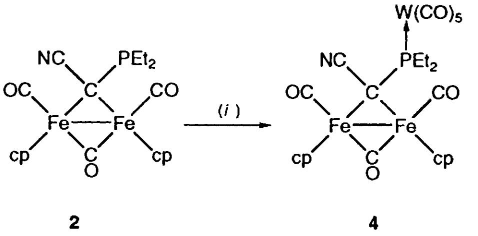
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.



Scheme 1 (*i*) $[W(CO)_5(thf)]$



Scheme 2



Scheme 3 (*i*) $[W(CO)_5(thf)]$

$(cp)_2(\mu\text{-CO})(\mu\text{-CNR}_2)][SO_3CF_3]$ (Scheme 2). Their nature has been ascertained spectroscopically. The driving force which accounts for the cyanide elimination, despite the different nature of the electrophilic reagents, might be attributed to the high stability of $[Fe_2(CO)_2(cp)_2(\mu\text{-CO})(\mu\text{-CNR}_2)]^+$ as a consequence of the μ-C–N double-bond formation [ν(CN) 1650–1550 cm^{-1}] and charge delocalization in the cationic complexes (see structural section). It is worth mentioning, as previously reported,[5] that abstraction of CN^- is easily reversed upon treatment with NBu_4CN (Scheme 2). However the tendency to μ-C–N multiple bond formation has been demonstrated to occur in the μ-cyanoalkylidenes $[Fe_2(CO)_2(cp)_2(\mu\text{-CO})\{\mu\text{-C(CN)(NHR)}\}]$ which upon treatment with triethylamine or on standing in solution (R = Ph) liberate HCN to give the stable isocyanide complexes $[Fe_2(CO)_3(cp)_2(CNR)]$.[1a]

The differences between the reactions reported in Scheme 1 and 2 are mechanistic in nature and depend on the electrophilic agents. In the $[W(CO)_5(thf)]$ case the formation of the anion provides the clue of the Lewis-acid addition centre. The reaction presumably proceeds *via* addition of $W(CO)_5$ to the N-nitrile atom of **1**, followed by cleavage of the μ-C–CN bond. The isocyanide intermediate $[CNW(CO)_5]^-$ thus formed is stabilized by co-ordination to a further $W(CO)_5$ fragment yielding the anion $[(OC)_5WCNW(CO)_5]^-$. Few anionic CN-bridged complexes are known[6] which have been usually prepared by treating anionic metal cyanides with Lewis-acid metal fragments.

By contrast, in the reaction of complex **1b** with HSO_3CF_3 a cationic intermediate has been detected by spectroscopy. The IR spectrum of the reaction mixture shows a band pattern [ν(CO) 2021, 1993 and 1829 cm^{-1}] similar but at higher frequencies to that of the precursor **1b** [ν(CO) 2004, 1970 and 1799 cm^{-1}]. Moreover a doublet at δ 3.49 (J_{HH} = 5.2 Hz), attributable to the Me groups, is observed in the ^{1}H NMR spectrum, suggesting that protonation has occurred at the nitrogen of the NMe_2 moiety to form the corresponding ammonium salt. It is worth mentioning that $[Fe_2(CO)_2(cp)_2(\mu\text{-CO})\{\mu\text{-C(CN)(NRMe}_2)\}]^+$ has been isolated (R = Me) or supposed to be the intermediate (R = H) in the reaction of $[Fe_2(CO)_2(cp)_2(\mu\text{-CO})\{\mu\text{-C(CN)(SMe}_2)\}][SO_3CF_3]$ with NMe_3 or $NHMe_2$, respectively.[1a] In this light and in view of the stability of the nitrilium cation $[Fe_2(CO)_2(cp)_2(\mu\text{-CO})\{\mu\text{-C(CNBu}^t)\text{H}\}]^+$,[7] it is reasonable to suppose that the methylation of **1a** and **1b** with $MeSO_3CF_3$ occurs at the CN nitrogen atom to form the corresponding cation which eliminates the isocyanide CNMe to give the observed cations **3**. However, although these reactions take about 8 h to complete, no intermediate adducts have been detected.

The reaction of the phosphinocarbene $[Fe_2(CO)_2(cp)_2(\mu\text{-CO})\{\mu\text{-C(CN)(PEt}_2)\}]$ **2** with equimolar amount of $[W(CO)_5(thf)]$ simply leads to the formation of the adduct $[Fe_2(cp)_2(CO)_2(\mu\text{-CO})\{\mu\text{-C(CN)[PEt}_2W(CO)_5]\}]$ **4** (Scheme 3). Compound **4** shows IR absorptions at 2071w, 1933vs and 1899 (sh) cm^{-1} due to the $W(CO)_5$ moiety, together with bands at 2002s, 1973w and 1810m cm^{-1} attributable to the iron carbonyls. These latter absorptions are shifted to higher wavenumbers with respect to those of the precursor $[Fe_2(CO)_2(cp)_2(\mu\text{-CO})\{\mu\text{-C(CN)(PEt}_2)\}]$ **2** (1996s, 1965w and 1806m cm^{-1}), an expected consequence of the co-ordination of the Lewis-acid fragment. The ^{13}C NMR spectrum of **4** demonstrates that the $W(CO)_5$ addition has occurred at the phosphorus atom since the $W\text{–}CO_{ax}$ are coupled (J_{PC} = 7 Hz). A single cp resonance is observed in both the ^{13}C and ^{1}H NMR spectra (δ 92.1 and 4.87 respectively) indicating that even in this case only one isomer, presumably the *cis*, bearing the CN group on the more hindered cp side of the molecule is present in solution.

Finally it is worth mentioning that protonation of complex **2** with HSO_3CF_3 has been reported[1b] to give, in an almost quantitative yield, the stable phosphonium complex $[Fe_2(CO)_2(cp)_2(\mu\text{-CO})\{\mu\text{-C(CN)(HPEt}_2)\}][SO_3CF_3]$ and that the reaction is promptly reversed upon treatment with tertiary amines. Therefore, no cyanide abstraction, upon treatment of **2** with acids, has been observed. The different behaviour of the μ-phosphinoalkylidene **2**, compared to the related μ-aminoalkylidene complexes **1**, may be attributed to the lower tendency of phosphorus, compared to nitrogen, toward π interaction with carbon.

Crystal and Molecular Structure of Complex **3a**.—The crystal contains well defined and ordered cations and anions. Perspective views of the molecular structure are shown in Figs. 1–3, and bond lengths and angles are listed in Table 1. An analysis of the shortest interion contacts shows that a preference for contacts among ions of opposite charge cannot be clearly evidenced, probably because the size and shape of the ions do not allow a simple salt-like arrangement. The shortest cation–

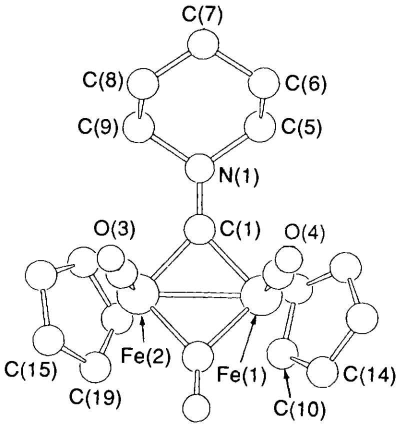


Fig. 1 The molecular structure of the cation in complex **3a** showing the atomic labelling scheme

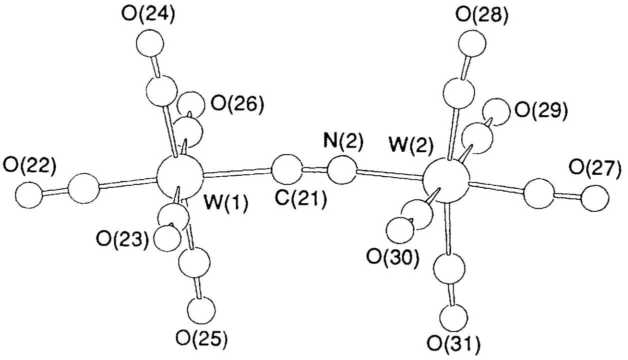


Fig. 2 The molecular structure of the anion in complex **3a** showing the atomic labelling scheme

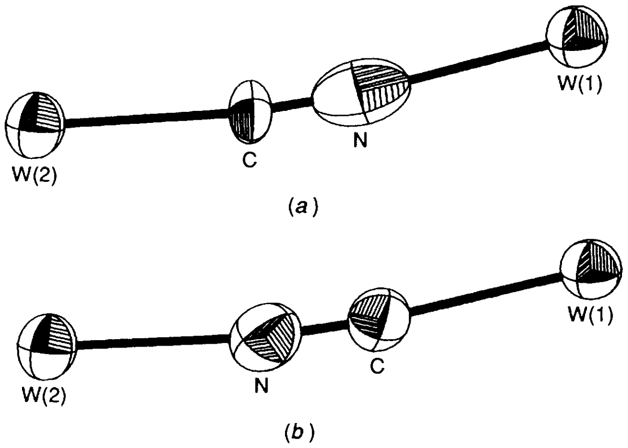


Fig. 3 Anisotropic thermal ellipsoids for the two structure models of the bridging CN^- ligand. Model (*a*) was discarded on the basis of the unrealistic orientation of the N atom ellipsoid

anion contacts have been found among the O atoms of the N-bonded $W(CO)_5$ moiety and the carbon atoms of the C_5H_5 ligands [O(27) ··· C(14) 3.15, O(28) ··· C(16) 3.06 Å]. This can be taken as an indication of unbalanced charge distribution in the anion to such an extent as to justify its ordered crystallization (see later).

The cation $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(NC_5H_{10})\}]^+$ consists of the usual $Fe_2(cp)_2(CO)_2$ unit in *cis* configuration and two bridging ligands, a CO molecule and a $CNC_5H_{10}{}^+$ iminium group containing the piperidine ring in a chair conformation and oriented on the side of the terminal CO ligands (Fig. 1). The ion conforms to approximate C_s symmetry.

Table 1 Selected bond lengths (Å) and angles (°) for $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)(\mu\text{-}CNC_5H_{10})][W_2(CO)_{10}(\mu\text{-}CN)]$ **3a**

Cation			
Fe(1)–Fe(2)	2.519(1)	N(1)–C(1)	1.280(8)
Fe(1)–C(1)	1.877(6)	N(1)–C(5)	1.487(7)
Fe(2)–C(1)	1.874(6)	N(1)–C(9)	1.501(8)
Fe(1)–C(2)	1.744(8)	C(5)–C(6)	1.51(1)
C(2)–O(2)	1.14(1)	C(6)–C(7)	1.49(1)
Fe(2)–C(3)	1.763(9)	C(7)–C(8)	1.49(1)
C(3)–O(3)	1.14(1)	C(8)–C(9)	1.51(1)
Fe(1)–C(4)	1.935(8)	Fe(1)–C(cp)$_{av}$	2.123(3)
Fe(2)–C(4)	1.925(8)	Fe(2)–C(cp)$_{av}$	2.117(9)
C(4)–O(4)	1.18(1)		
C(9)–N(1)–C(1)	124.2(6)	Fe(1)–C(1)–N(1)	138.5(5)
C(9)–N(1)–C(5)	111.1(6)	Fe(2)–C(1)–N(1)	136.7(5)
C(1)–N(1)–C(5)	124.6(5)		
Anion			
W(1)–C(22)	2.003(9)	W(2)–N(2)	2.187(7)
C(22)–O(22)	1.14(1)	W(2)–C(27)	1.955(9)
W(1)–C(23)	2.003(8)	C(27)–O(27)	1.17(1)
C(23)–O(23)	1.16(1)	W(2)–C(28)	2.011(8)
W(1)–C(24)	2.016(9)	C(28)–O(28)	1.14(1)
C(24)–O(24)	1.13(1)	W(2)–C(29)	2.041(10)
W(1)–C(25)	2.036(8)	C(29)–O(29)	1.13(1)
C(25)–O(25)	1.14(1)	W(2)–C(30)	2.036(8)
W(1)–C(26)	2.024(8)	C(30)–O(30)	1.13(1)
C(26)–O(26)	1.14(1)	W(2)–C(31)	2.043(10)
W(1)–C(21)	2.184(8)	C(31)–O(31)	1.13(1)
N(2)–C(21)	1.15(1)		

The Fe–Fe distance is normal [2.519(1) Å], and is scarcely influenced by the nature of the bridging groups. The two bridging carbons exhibit average distances of 1.930(6) and 1.875(6) Å for Fe–C(O) and Fe–C(N), respectively. The difference can be explained in terms of a different use of the p_π orbitals of these atoms. For the bridging CO, as is usual, both orbitals are primarily engaged in multiple bonding to oxygen [C–O 1.18(1) Å]. The bonds of the μ-C(N) atom, C(1), are different. Only one p_π orbital can be engaged in multiple bonding to the sp^2-hybridized N(1), therefore the in-plane p_π orbital is exclusively used in the bond to the diiron system. The C(1)–N(1) distance [1.280(8) Å] is normal for a double bond and fits well with the single bonds N(1)–C(5) and N(1)–C(9) [average 1.49(1) Å]. Comparable values have been found in the recently reported cation *cis*-$[Re_2(cp)_2(CO)(CNMe)(\mu\text{-}CO)(\mu\text{-}CNMe_2)]^+$,[4b] in which the μ-C–Fe and μ-C–N distances are 1.86(1) and 1.303(7) Å, respectively. The π bonds around C(1) constitute an efficient mechanism of charge delocalization and stabilization of the cation, as confirmed by extended-Hückel calculations of the charge distribution. In particular, the charges calculated for the carbons around the iminium nitrogen are: +0.07 at C(1) and +0.086 e at C(5) and C(9). The nitrogen itself bears a charge of −0.038 e. Carbons and hydrogens in the cp groups bear an average charge of +0.02 e. The lower charge at C(1) with respect to the CH_2 groups bonded to N(1) confirms the efficiency of Fe-to-μ-C(1) back bonding.

The anion $[(OC)_5WCNW(CO)_5]^-$ is depicted in Fig. 2. It consists of two $W(CO)_5$ fragments joined by a bridging cyanide ligand for which we have been able to tell which is carbon and which is nitrogen (see Experimental section). The study of this anion provides a good opportunity to compare the bonding abilities of the C and N ends of the cyanide group bridging identical moieties in a finite molecule. The $W(CO)_5$ groups face each other in eclipsed configuration and the anion as a whole can be attributed a C_{4v} idealized symmetry. The observed configuration shows that both $W(CO)_5$ groups interact, from opposite sides, with the same sets of π orbitals of the CN^- ligand. The atoms W(1), C(21), N(2), W(2) and two CO ligands are almost collinear with angles at C(21) and N(2) of 175.6(6) and 172.9(7)°, respectively. The deviations from strict linearity can be attributed to asymmetry of the packing forces and are present also in the few species in which the bridging cyanide group has been found ordered, *e.g.* 172.4(3) and 159.8(3)° in $[(CN)_5CoCNCo(NH_3)_5]$,[8] 168(1) and 171(1)° in $[(OC)_3(phen)MnCNMn(phen)(CO)_3]^+$ (phen = 1,10-phenanthroline)[9] and 175(1) and 168(1)° in $[(cp)(dppe)RuCNRu(PPh_3)_2(cp)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$).[10]

The C–N distance [1.15(1) Å] is equal to that found[11] in $[(PhMe_2P)_3Cl_2IrCNIrCl_2(PMe_2Ph)_3]^+$ and in $[W(CO)_5(NCCH_2CO_2H)]$[12] and in good agreement with other recently reported values.[13] The W(1)–C(21) distance [2.184(8) Å] is in very good agreement with the average W–C(N) value [2.19(1) Å] recently reported[14] for the anion $[Ni\{NCW(CO)_5\}_5]^{3-}$, but is longer than that in the isonitrile derivatives $[(OC)_5W\{CNCH_2CHC(CPh_2)N(Ph)C\}W(CO)_5(NH)]$ [2.12(1) Å][15] and $[MeC\{CH_2NCW(CO)_5\}_3]$ [2.08 and 2.11(1) Å].[16]

The W(2)–N(2) distance [2.187(7) Å] agrees well with the values found in the nitrile derivatives $[W(CO)_5(NCCH_2CO_2H)]$ [2.178(7) Å][12] and $[(OC)_5WNCCFe_3(cp)_3(\mu\text{-}CO)_3]$ [2.16(1) Å].[17] The fact that W(1)–C(21) and W(2)–N(2) are equal within experimental error (average 2.18 Å), in spite of the smaller size of the nitrogen atom, can be ascribed to a combination of the levelling effect of the anionic charge and the stronger bonding ability of the carbon side. However the non-equivalence of these interactions is evidenced in the CO groups *trans* to them. The distances in the sequence W(1)–C(22)–O(22), *trans* to C(21) [2.00(1), 1.14(1) Å], are different from those in W(2)–C(27)–O(27), *trans* to N(2) [1.95(1), 1.17(1) Å]. A plausible explanation is in terms of the lower π-accepting ability of the more negative N(2) which allows the implied W(2) orbitals better to back-donate to the C(27)–O(27) group. The σ and π interactions along the molecular axis provide a good mechanism of distribution of the anionic charge, but a significant polarity is maintained along the axis, as the ordered crystallization of the anion clearly indicates.

It is worth mentioning that extended-Hückel calculations of the charge distribution in the anion are in accord with the proposed rationalizations and the information contained in the crystal packing. The charges calculated for the oxygen atoms range from −0.19 to −0.25 e, the most negative being attributed to O(27), in accord with the experimental findings. Finally, the carbon of the CN group is substantially neutral, while a value of −0.13 e is calculated for the N(2) atom.

Experimental

General Procedures.—All reactions were routinely carried out under nitrogen by standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Instruments employed: IR, Perkin Elmer 983-G; NMR, Varian Gemini 200. Elemental analyses were by Pascher Microanalytical Laboratory (Remagen, Germany). The compounds $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)(SMe_2)\}][SO_3CF_3]$,[2] $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)(NMe_2)\}]$ **1b**[1a] and $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)(PEt_2)\}]$ **2**[1b] were prepared according to published methods.

Preparations.—$[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)(NC_5H_{10})\}]$ **1a**. Piperidine (0.10 cm^3, 1.01 mmol) was added to a stirred solution of $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)(SMe_2)\}][SO_3CF_3]$ (0.30 g, 0.52 mmol) in MeCN (20 cm^3). The mixture was stirred for 15 min and the solvent removed *in vacuo*. The residue was dissolved in dichloromethane and filtered on an alumina column (3 × 5 cm). The red solution was evaporated to minimum volume, layered with pentane and crystallized at −20 °C to yield 0.13 g (56%) of complex **1a**, m.p. 140–142 °C (decomp.) (Found: C, 53.35; H, 4.60. $C_{20}H_{20}Fe_2N_2O_3$ requires C, 53.60; H, 4.50%). IR (CH_2Cl_2): ν_{max} 2147w (CN), 2005s, 1971w (CO) and 1822m cm^{-1} (μ-CO). NMR (CD_2Cl_2): δ_H 4.76 (10 H, s, cp), 3.15 [4 H, m, $NCH_2(CH_2)_3CH_2$] and 1.52 [6 H, m, $NCH_2(CH_2)_3CH_2$]; δ_C 268.9 (μ-CO), 211.2 (CO), 162.4 (μ-C), 128.3 (CN), 91.2 (cp), 60.1, 27.2 and 25.2 (NC_5H_{10}).

$[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(NC_5H_{10})\}][(OC)_5WCNW(CO)_5]$ **3a**. Complex **1a** (0.30 g, 0.67 mmol) was dissolved in thf (20 cm^3) and treated with a slight excess of $[W(CO)_5(thf)]$ (0.80 mmol) obtained by photolysis of $[W(CO)_6]$ (0.70 g, 2.00 mmol) in tetrahydrofuran (25 cm^3). The reaction mixture was stirred for 2 h, then $[W(CO)_5(thf)]$ (0.80 mmol) was added and the mixture stirred for 1 h. The volatile material was then removed under vacuum and the residue washed with hexane, redissolved in CH_2Cl_2 and filtered through an alumina column. The red-orange solution was collected, reduced to minimum volume and layered with pentane at −20 °C affording red crystals of complex **3a** (0.26 g, 35%), m.p. 129–130 °C (decomp.) (Found: C, 32.85; H, 1.85. $C_{30}H_{20}Fe_2N_2O_{13}W_2$ requires C, 32.90; H, 1.85%). IR (CH_2Cl_2): ν_{max} 2123w (W–CN), 2029s, 1983 (sh) (Fe–CO), 2059w, 1936vs, 1875 (sh) (W–CO), 1845 (sh) (μ-CO) and 1572w cm^{-1} (C=N). NMR (CD_2Cl_2): δ_H 5.16 (10 H, s, cp), 4.55 [4 H, m, $NCH_2(CH_2)_3CH_2$] and 2.14–1.75 [6 H, m, $NCH_2(CH_2)_3CH_2$]; $\delta_C(CD_2Cl_2)$ 315.3 (μ-C), 253.6 (μ-CO), 208.2 (Fe–CO), 202.9 (W–CO$_{ax}$, J_{WC} = 151), 201.1 (W–CO$_{ax}$, J_{WC} = 141), 199.0 (W–CO$_{eq}$, J_{WC} = 129), 198.0 (W–CO$_{eq}$, J_{WC} = 125), 153.4 (CN, J_{WC} = 99 Hz), 90.2 (cp), 66.8, 27.6 and 23.6 (NC_5H_{10}).

$[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)][(OC)_5WCNW(CO)_5]$ **3b**. A solution of complex **1b** (0.30 g, 0.73 mmol) in thf (20 cm^3) was treated with $[W(CO)_5(thf)]$ as described for **3a** yielding **3b** as red crystals (0.16 g, 21%), m.p. 136–138 °C (decomp.) (Found: C, 30.50; H, 1.80. $C_{27}H_{16}Fe_2N_2O_{13}W_2$ requires C, 30.70; H, 1.50%). IR (CH_2Cl_2): ν_{max} 2124w (W–CN), 2032s, 1990 (sh) (Fe–CO), 2059w, 1934vs, 1862 (sh) (W–CO), 1840 (sh) (μ-CO) and 1606w cm^{-1} (C=N). ^1H NMR (CD_2Cl_2): δ 5.17 (10 H, s, cp) and 4.18 (6 H, s, Me).

$[Fe_2(cp)_2(CO)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)[PEt_2W(CO)_5]\}]$ **4**. Complex **2** (0.30 g, 0.66 mmol) was dissolved in thf (20 cm^3) and treated with an equimolar amount of $[W(CO)_5(thf)]$ obtained by photolysis of $[W(CO)_6]$ in tetrahydrofuran. The mixture was stirred for 2 h and dried under vacuum. The residue, dissolved in CH_2Cl_2, was chromatographed on an alumina column. Elution with CH_2Cl_2 gave a reddish brown fraction which was collected and evaporated to dryness. Recrystallization of the residue from CH_2Cl_2 layered with pentane at − 20 °C gave red crystals of **4** (0.27 g, 53%), m.p. 128–130 °C (decomp.) (Found: C, 37.50; H, 2.80. $C_{24}H_{20}Fe_2NO_8PW$ requires C, 37.10; H, 2.60%). IR (CH_2Cl_2): ν_{max} 2165w (CN), 2002s, 1973m (Fe–CO), 2071w, 1933vs, 1899 (sh) (W–CO) and 1810m cm^{-1} (μ-CO). NMR: $\delta_H(CDCl_3)$ 4.87 (10 H, s, cp), 1.96 (4 H, q, J_{HH} = 7.6, PCH_2CH_3) and 1.28 (6 H, d of t, J_{PH} = 14.6, PCH_2CH_3); $\delta_C(CD_2Cl_2)$ 258.5 (μ-CO), 211.7 (Fe–CO, J_{PC} = 4), 199.4 (W–CO$_{ax}$, J_{PC} = 7, J_{WC} = 125), 197.5 (W–CO$_{eq}$, J_{WC} = 130 Hz), 142.4 (CN, J_{PC} = 11), 114.5 (μ-C, J_{PC} = 3), 92.1 (cp), 31.5 (PCH_2CH_3, J_{PC} = 21 Hz) and 11.4 (PCH_2CH_3).

Reaction of $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)(NC_5H_{10})\}]$ **1a** *with* $MeSO_3CF_3$.—A slight excess of $MeSO_3CF_3$ (0.16 g, 0.36 mmol) was added to a dichloromethane solution (20 cm^3) of complex **1a** (0.15 g, 0.33 mmol), and the mixture was stirred for 8 h. Addition of Et_2O gave a microcrystalline solid which was filtered off, washed with Et_2O and recrystallized from CH_2Cl_2 layered with Et_2O yielding $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(NC_5H_{10})\}][SO_3CF_3]$ (0.06 g, 32%). IR (MeCN): ν_{max} 2021s, 1988w (Fe–CO), 1835m (μ-CO) and 1595w (C=N). ^1H NMR (CD_3CN): δ 5.33 (10 H, s, cp), 4.60 [4 H, m, $NCH_2(CH_2)_3CH_2$] and 2.00 [6 H, m, $NCH_2(CH_2)_3CH_2$].

Reactions of $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(CN)(NMe_2)\}]$ **1b**—*With* $MeSO_3CF_3$. Complex **1b** was treated with $MeSO_3CF_3$ as above described yielding $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(NMe_2)\}]SO_3CF_3$ (38%) identified by comparison of its spectroscopic properties with those reported.[4b]

With HSO_3CF_3. A solution of complex **1b** (0.10 g, 0.24 mmol) in CH_2Cl_2 (10 cm^3) was treated with HSO_3CF_3 (0.05 cm^3, 0.57 mmol) and the mixture stirred for 15 min. The IR spectrum of the mixture showed absorptions at 2021s, 1993w and 1829m cm^{-1}. Upon standing in solution (4–8 h) the compound $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)(\mu\text{-}CNMe_2)][SO_3CF_3]$ was formed in about 70% yield. When equimolar amounts of HSO_3CF_3 were added to a sample of **1b** dissolved in CD_2Cl_2 in a NMR tube and the ^1H NMR spectrum immediately recorded, the following resonances were observed: δ_H 5.22 (10 H, s, cp), 3.49 (6 H, d, J_{HH} = 5.2 Hz, NMe) and 5.8 (1 H, br, NH).

Table 2 Crystal data and experimental details for complex **3a**

Formula	$C_{30}H_{20}Fe_2N_2O_{13}W_2$
M	1095.9
Crystal size/mm	0.15 × 0.40 × 0.35
System	Monoclinic
Space group	$P2_1/n$ (no. 14)
a/Å	11.196(3)
b/Å	17.389(3)
c/Å	17.938(3)
β/°	95.19(2)
U/Å^3	3478.2
Z	4
D_c/g cm^{-3}	2.09
F(000)	2072
Radiation (graphite-monochromated) (λ/Å)	Mo-Kα (0.710 67)
μ(Mo-Kα)/cm^{-1}	71.6
Scan mode	ω
θ limits/°	2–23
ω scan width/°	$0.9 + 0.35 \tan\theta$
Prescan rate/° min^{-1}	4
Prescan acceptance, $\sigma(I)/I$	0.5
Required $\sigma(I)/I$	0.02
Maximum scan time/s	120
Standard reflections	3, measured periodically
Reflections collected	4728
Unique observed reflections, N_o $[F_o > 4\sigma(F_o)]$	3939
No. of refined parameters, N_p	443
R,[a] R'[b]	0.0323, 0.0346
K, g[c]	0.256, 5.0×10^{-4}
Quality-of-fit indicator[d]	0.86

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{\frac{1}{2}}$. [c] $w = K/[\sigma^2(F) + |g|F^2]$. [d] Quality-of-fit $= [\Sigma w(F_o - F_c)^2/(N_o - N_p)]^{\frac{1}{2}}$.

Structure Determination of Complex **3a**.—Crystal data and details of the data collection for $[Fe_2(CO)_2(cp)_2(\mu\text{-}CO)\{\mu\text{-}C(NC_5H_{10})\}][(OC)_5WCNW(CO)_5]$ **3a** are given in Table 2. The diffraction experiments were carried out at room temperature on an Enraf-Nonius CAD-4 diffractometer. The unit-cell parameters were determined from 25 randomly selected strong reflections by using automatic search, indexing and least-squares routines. Data were corrected for Lorentz and polarization effects. No decay correction was necessary; an absorption correction was applied on the basis of azimuthal scan data.[18] All calculations were performed using the SHELX 76 package of programs.[19] The metal atom positions were determined by direct methods and all non-hydrogen atoms located from Fourier-difference syntheses. The cyclopentadienyl rings were treated as rigid groups (C–C 1.42 Å). The hydrogen atoms were added in calculated positions (C–H 0.90 Å) and their coordinates not refined but continuously updated with respect to their carbon atoms.

A point of both chemical and crystallographic interest was the structure of the $[(OC)_5WCNW(CO)_5]^-$ anion in which the orientation of the bridging CN group seemed hardly discernible as a consequence of disorder or inability to discriminate carbon from nitrogen in the vicinity of two tungsten atoms. Nevertheless a refinement of either structure model was tried. No clue could be drawn from the R indices, but some evidence of which was the wrong model was given by the isotropic refinement of the thermal motion; unreasonably different thermal parameters were obtained for the assumed C and N atoms. Anisotropic refinements strengthened this evidence as the wrong nitrogen exhibited a thermal ellipsoid markedly elongated along the bond axis (Fig. 3). The well behaved model was therefore accepted as the true one, and the refinement completed using anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were assigned fixed thermal parameters of 0.08 Å^2. The final Fourier-difference map showed peaks not exceeding 1.06 e Å^{-3} in the vicinity of the W atoms. Positional parameters with their estimated standard deviations corresponding to the final least-squares refinement cycle are given in Table 3.

Table 3 Fractional atomic coordinates for complex **3a**

Atom	x	y	z
W(1)	0.231 85(3)	0.119 10(2)	−0.001 20(2)
W(2)	−0.200 85(3)	0.224 35(2)	−0.131 64(2)
Fe(1)	−0.225 11(8)	0.581 00(5)	0.176 96(5)
Fe(2)	−0.372 46(8)	0.472 90(6)	0.149 93(6)
C(1)	−0.206 7(6)	0.473 7(4)	0.176 4(3)
C(2)	−0.156 0(7)	0.584 7(5)	0.093 7(4)
O(2)	−0.111 1(7)	0.586 3(5)	0.039 4(4)
C(3)	−0.343 8(7)	0.448 4(5)	0.057 8(5)
O(3)	−0.323 8(7)	0.431 0(5)	−0.001 1(4)
C(4)	−0.379 0(7)	0.578 8(4)	0.118 4(4)
O(4)	−0.445 0(5)	0.620 2(3)	0.082 9(4)
N(1)	−0.121 8(5)	0.424 2(3)	0.182 8(3)
C(5)	0.006 5(6)	0.442 8(5)	0.203 6(4)
C(6)	0.083 5(7)	0.416 5(5)	0.143 7(5)
C(7)	0.067 7(8)	0.332 7(4)	0.127 7(5)
C(8)	−0.060 6(8)	0.313 4(5)	0.108 2(5)
C(9)	−0.138 5(7)	0.339 8(4)	0.167 6(5)
C(10)	−0.299 0(5)	0.639 6(4)	0.266 3(3)
C(11)	−0.195 4(5)	0.598 2(4)	0.294 8(3)
C(12)	−0.096 2(5)	0.626 6(4)	0.259 1(3)
C(13)	−0.138 4(5)	0.685 5(4)	0.208 6(3)
C(14)	−0.263 7(5)	0.693 6(4)	0.213 1(3)
C(15)	−0.548 6(5)	0.431 7(5)	0.139 1(3)
C(16)	−0.469 6(5)	0.371 4(5)	0.164 5(3)
C(17)	−0.411 6(5)	0.393 3(5)	0.235 0(3)
C(18)	−0.454 8(5)	0.467 2(5)	0.253 1(3)
C(19)	−0.539 4(5)	0.490 9(5)	0.193 8(3)
N(2)	−0.020 4(6)	0.193 0(4)	−0.084 6(4)
C(21)	0.069 4(7)	0.169 5(4)	−0.057 6(4)
C(22)	0.376 5(8)	0.071 6(5)	0.054 5(5)
O(22)	0.457 3(7)	0.042 5(5)	0.085 4(4)
C(23)	0.162 1(7)	0.015 0(5)	−0.025 3(5)
O(23)	0.127 7(7)	−0.046 4(4)	−0.042 1(5)
C(24)	0.317 6(8)	0.115 2(5)	−0.095 2(5)
O(24)	0.368 4(8)	0.112 6(5)	−0.146 6(4)
C(25)	0.150 0(8)	0.120 5(4)	0.095 6(5)
O(25)	0.108 1(7)	0.122 0(4)	0.151 5(4)
C(26)	0.303 1(8)	0.224 6(5)	0.020 8(5)
O(26)	0.345 1(8)	0.283 7(4)	0.032 1(4)
C(27)	−0.364 8(8)	0.249 6(5)	−0.170 9(5)
O(27)	−0.461 1(5)	0.266 3(5)	−0.197 0(4)
C(28)	−0.159 7(7)	0.241 5(5)	−0.237 2(4)
O(28)	−0.143 2(6)	0.256 2(4)	−0.297 6(4)
C(29)	−0.169 0(8)	0.339 3(5)	−0.118 0(5)
O(29)	−0.153 9(8)	0.403 3(4)	−0.115 9(6)
C(30)	−0.229 3(8)	0.110 9(5)	−0.155 1(5)
O(30)	−0.241 2(7)	0.048 1(4)	−0.170 3(4)
C(31)	−0.266 9(10)	0.215 0(7)	−0.029 5(6)
O(31)	−0.309 8(8)	0.210 6(7)	0.024 9(5)

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

Extended-Hückel molecular orbital calculations[20] were carried out separately on the experimental structures of the two ions present in the asymmetric unit using the modified Wolfberg–Helmholz formula.[21] Standard atomic parameters were used for C, O, N and H, while those for Fe and W were taken from the literature.[22,23] A self-consistent charge calculation was performed assuming a quadratic dependence of H_{ii} on charge.

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