Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 42.[1] Synthesis of the Compounds $[N(PPh_3)_2][Fe_2W(\mu\text{-}CO)(\mu\text{-}NO)(\mu_3\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)]$ (R = Me or C_6H_4Me-4) and the *X*-Ray Crystal Structure of the Tolylmethylidyne Complex†

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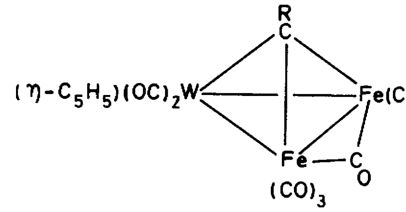
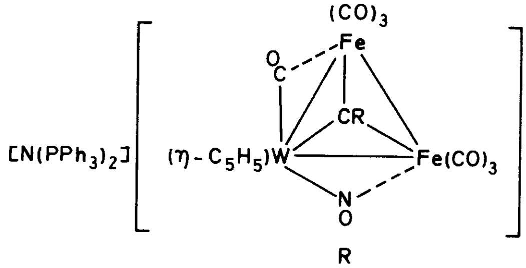
The compounds $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (R = Me or C_6H_4Me-4) and $[N(PPh_3)_2][NO_2]$ react in tetrahydrofuran at room temperature to afford the salts $[N(PPh_3)_2][Fe_2W(\mu\text{-}CO)(\mu\text{-}NO)(\mu_3\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)]$. An *X*-ray diffraction study was carried out on the species with R = C_6H_4Me-4, which crystallises with a molecule of tetrahydrofuran. The anion contains an essentially isosceles triangle of metal atoms [Fe–W 2.702(2) and 2.716(2), Fe–Fe 2.607(3) Å], capped by the CC_6H_4Me-4 group [μ_3-C–Fe 1.969(13) and 2.008(10), μ_3-C–W 2.055(11) Å]. Each iron atom carries three terminally bound CO molecules. The tungsten atom is bonded by the cyclopentadienyl ligand, and in addition is attached to a CO and an NO group. These carbonyl and nitrosyl groups asymmetrically bridge the two Fe–W edges of the metal triangle [W–C–O 160.0(9), W–N–O 157.0(10)°]. Protonation of the salt $[N(PPh_3)_2][Fe_2W(\mu\text{-}CO)(\mu\text{-}NO)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)]$ with $HBF_4\cdot Et_2O$ affords the di-irontungsten complex $[Fe_2W(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}NOH)(CO)_7(\eta\text{-}C_5H_5)]$. A structurally related species $[Fe_2W(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}NC_6H_4Me\text{-}4)(CO)_7(\eta\text{-}C_5H_5)]$ is obtained by heating a mixture of $[Fe_2W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ with $MeC_6H_4N_3$-4 in tetrahydrofuran. Spectroscopic data (i.r. and n.m.r.) for the new complexes are reported and discussed.

The alkylidynetungsten complexes $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = Me or C_6H_4Me-4) react with excess of $[Fe_2(CO)_9]$ to afford the trimetal cluster compounds $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (**1**).[2,3] The reactivity of these clusters is of interest, and we are currently studying the effect of various reagents on these species, and on other heteronuclear trimetal compounds with capping alkylidyne ligands. We have earlier described reactions of the di-irontungsten complexes with tertiary phosphines, alkynes, and elemental sulphur and selenium. Not surprisingly, tertiary phosphines displace CO ligands.[2] This process also occurs with alkynes, but in a subsequent reaction an iron carbonyl fragment is displaced, and dimetal compounds $[FeW(\mu\text{-}CRCR^1CR^2)(CO)_5(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4, R^1 or R^2 = alkyl or aryl) are produced.[4] The latter species result from a coupling of the tolylmethylidyne group with the alkynes, leading to C–C bond formation. The alkylidyne ligands are also reactive centres in reactions of the trimetal clusters (**1**) with sulphur or selenium.[3] Compounds of formulation $[Fe_2W(\mu\text{-}CR)(\mu_3\text{-}E)(CO)_7(\eta\text{-}C_5H_5)]$ (E = S or Se) are obtained, with the alkylidyne group shifting from a triply-bridging site in the precursors to an edge-bridging site in the products. Isolation of $[Fe_2W(\mu_3\text{-}SCMe)(CO)_8(\eta\text{-}C_5H_5)]$, as well as $[Fe_2W(\mu\text{-}CMe)(\mu_3\text{-}S)(CO)_7(\eta\text{-}C_5H_5)]$, in the reaction of sulphur with (**1b**), and the discovery that the thio-acyl species releases CO to give $[Fe_2W(\mu\text{-}CMe)(\mu_3\text{-}S)(CO)_7(\eta\text{-}C_5H_5)]$, indicated that these interesting μ_3-CR to μ-CR transformations proceed *via* the intermediacy of di-irontungsten complexes containing μ_3-ECR ligands. The reactions described in this paper were designed to extend our knowledge of the reactivity of the clusters (**1**). The reagent $[N(PPh_3)_2][NO_2]$ was chosen for study in the expectation that it would introduce an NO group into the trimetal system.[5]



R	
(**1a**)	C_6H_4Me-4
(**1b**)	Me



R	
(**2a**)	C_6H_4Me-4
(**2b**)	Me

Results and Discussion

Treatment of the compounds (**1**) with $[N(PPh_3)_2][NO_2]$ in tetrahydrofuran (thf) at room temperature produces dark red crystalline salts $[N(PPh_3)_2][Fe_2W(\mu\text{-}CO)(\mu\text{-}NO)(\mu_3\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)]$ (**2**). The i.r. spectra showed several carbonyl

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† Bis(triphenylphosphine)iminium 1,3-μ-carbonyl-1,1,1,2,2,2-hexacarbonyl-3-η^5-cyclopentadienyl-2,3-μ-nitrosyl-μ_3-*p*-tolylmethylidyne-*triangulo*-di-irontungsten.

Supplementary data available (No. SUP 56452, 6 pp.): full listing of bond distances and angles, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Selected internuclear distances (Å) and angles (°) for $[N(PPh_3)_2][Fe_2W(\mu\text{-}CO)(\mu\text{-}NO)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)]\cdot$thf (**2a**)*

W–Fe(1)	2.716(2)	W–Fe(2)	2.702(2)	Fe(2)–C(1)	2.008(10)	Fe(2)–N(1)	2.286(12)
W–C(1)	2.055(11)	W–C(11)	2.322(10)	Fe(2)–C(2)	1.768(19)	Fe(2)–C(3)	1.746(17)
W–C(12)	2.347(14)	W–C(13)	2.358(14)	Fe(2)–C(4)	1.797(13)	C(1)–C(21)	1.493(13)
W–C(14)	2.339(13)	W–C(15)	2.317(13)	C(27)–C(24)	1.593(14)	N(1)–O(1)	1.218(14)
W–N(1)	1.911(11)	W–C(5)	1.871(14)	C(2)–O(2)	1.146(25)	C(3)–O(3)	1.174(22)
Fe(1)–Fe(2)	2.607(3)	Fe(1)–C(1)	1.969(13)	C(4)–O(4)	1.167(16)	C(5)–O(5)	1.207(20)
Fe(1)–C(5)	2.332(12)	Fe(1)–C(6)	1.747(15)	C(6)–O(6)	1.147(19)	C(7)–O(7)	1.165(19)
Fe(1)–C(7)	1.754(16)	Fe(1)–C(8)	1.778(13)	C(8)–O(8)	1.170(15)		

Fe(1)–W–Fe(2)	57.5(1)	Fe(1)–W–C(1)	46.2(4)	Fe(2)–W–C(1)	47.6(3)	Fe(1)–W–N(1)	94.9(3)
Fe(2)–W–N(1)	94.9(3)	Fe(1)–W–C(5)	57.6(3)	Fe(2)–W–C(5)	100.4(4)	N(1)–W–C(5)	89.8(6)
W–Fe(1)–C(1)	48.9(3)	Fe(2)–Fe(1)–C(1)	49.7(3)	W–Fe(1)–C(5)	42.7(3)	Fe(2)–Fe(1)–C(5)	91.8(3)
W–Fe(2)–Fe(1)	61.5(1)	W–Fe(2)–C(1)	49.1(3)	Fe(1)–Fe(2)–C(1)	48.4(4)	W–Fe(2)–N(1)	44.1(3)
Fe(1)–Fe(2)–N(1)	89.5(4)	W–C(1)–Fe(1)	84.9(5)	W–C(1)–Fe(2)	83.3(4)	Fe(1)–C(1)–Fe(2)	81.9(4)
W–C(1)–C(21)	131.5(6)	Fe(1)–C(1)–C(21)	130.0(7)	Fe(2)–C(1)–C(21)	127.8(9)	W–N(1)–Fe(2)	79.6(4)
W–N(1)–O(1)	157.0(10)	Fe(2)–N(1)–O(1)	123.0(9)	W–C(5)–Fe(1)	79.7(5)	W–C(5)–O(5)	160.0(9)
Fe(1)–C(5)–O(5)	120.2(8)	Range Fe–C–O	175(2)—180(1)	Range OC–Fe–CO	87.8(9)—104.5(7)		

* For the cation $[N(PPh_3)_2]^+$, N–P (mean) 1.58 Å, P–N–P 140.6(5)°.

stretching bands, including one at low frequency [1 801 (**2a**), 1 797 cm^{-1} (**2b**)], corresponding to the presence of a semi-bridging carbonyl ligand. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of both salts (**2**) clearly revealed the presence of triply-bridging alkylidyne groups with resonances at δ 275.6 (**2a**) and 277.7 p.p.m. (**2b**). These chemical shifts may be compared with those observed for the ligated carbon atoms in (**1a**) (285.9 p.p.m.) and (**1b**) (282.6 p.p.m.), and their occurrence below *ca.* 300 p.p.m. is in in accord with the alkylidyne ligand capping rather than edge-bridging a metal triangle.[2,6,7] The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of (**2**) in the CO resonance region were also informative. That for (**2b**) showed signals at δ 251.8 (WCO), 226.7 (2 FeCO), and 218.2 p.p.m. (4 FeCO), indicating that site-exchange of the carbonyl groups on iron occurs at room temperature. In contrast, the spectrum of (**2a**) has four resonances for the FeCO groups [δ 225.0 (1 CO), 221.1 (2 CO), 217.7 (2 CO), and 214.4 p.p.m. (1 CO)], indicating a partial slowing down of exchange processes. Moreover, the signal at δ 246.7 for the tungsten ligated carbonyl group shows ^{183}W coupling [*J*(WC) 122 Hz].

No bands in the i.r. spectra of (**2**) could be unambiguously assigned to the NO ligand. In the salts $[N(PPh_3)_2][M_3(CO)_{10}(NO)]$ (M = Ru or Os) the NO absorptions are masked by those of the cation.[5] However, elemental analyses of (**2**) showed that nitrogen was present and agreed with the formulation of the salts. In order to establish firmly the structures, an *X*-ray diffraction study was carried out on (**2a**). The anion is shown in the Figure, and important internuclear separations and angles are given in Table 1.

As anticipated, the core of the anion is an essentially isosceles triangle of Fe_2W atoms capped by the CC_6H_4Me-4 ligand. The metal–metal separations [Fe–Fe 2.607(3), Fe–W 2.716(2) and 2.702(2) Å] may be compared with those in (**1a**) [Fe–Fe 2.538(2), Fe–W 2.756(2) and 2.805(2) Å].[2] The small differences observed may be attributed to a different arrangement of edge-bridging ligands in the two structures. Thus in (**1a**) the Fe–Fe vector has a CO bridge which is absent from this triangular edge in (**2a**), leading to a somewhat longer separation in the latter. The μ_3-C atom in (**2a**) is, as expected, somewhat more closely linked with the iron atoms [1.969(13) and 2.008(10) Å] than with the tungsten [2.055(11) Å]. A similar feature is seen in (**1a**) [μ_3-C–Fe 1.969(13) and 2.008(10), and μ_3-C–W 2.055(11) Å].[2] In (**2a**) each iron atom is ligated by three essentially linear and orthogonal CO groups. The tungsten atom carries the η-C_5H_5 ring, as expected. The Fe–W edges of the cluster are asymmetrically bridged by CO and NO groups attached to the tungsten and weakly bound to the iron atoms [W–C(5)–O(5) 160.0(9), W–N(1)–O(1) 157.0(10) Å]. Since the CO and NO groups occupy *pseudo* mirror symmetric sites in the anion it is possible that they are disordered in the solid-state structure (see Experimental section).

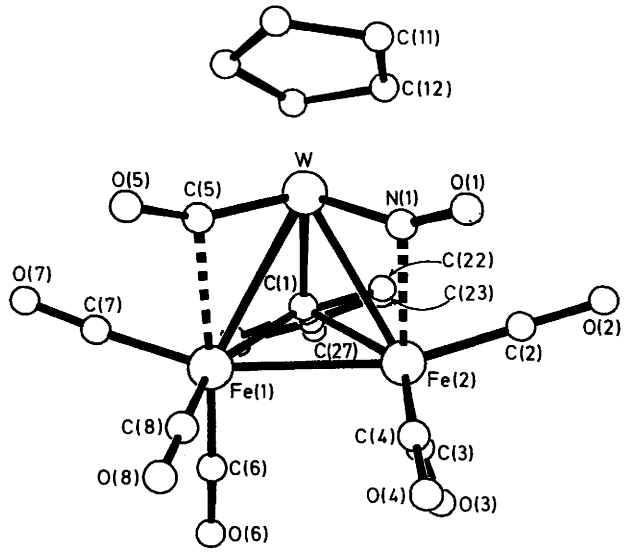
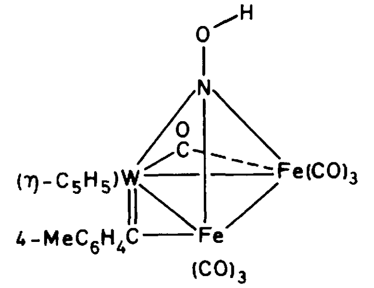


Figure. Molecular structure of the anion of $[N(PPh_3)_2][Fe_2W(\mu\text{-}CO)(\mu\text{-}NO)(\mu_3\text{-}C_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)]\cdot$thf (**2a**) showing the atom numbering scheme

The cation of (**2a**) has a bent P–N–P [140.6(5) Å] structure. Both bent and linear arrangements of the P–N–P spine have been found in salts of the cation $[N(PPh_3)_2]^+$.[8]

Although no reaction was observed between the salt (**2a**) and $[AuCl(PPh_3)]$, in the presence of $TlBF_4$ or $AgBF_4$, the compound was successfully protonated. Treatment of dichloromethane solutions of (**2a**) at −50 °C with $HBF_4\cdot Et_2O$ afforded a dark red crystalline compound $[Fe_2W(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(\mu_3\text{-}NOH)(CO)_6(\eta\text{-}C_5H_5)]$ (**3**). The formulation for (**3**) is based on microanalysis, and on spectroscopic data, discussed below. Stevens and Gladfelter[9] have reported that protonation



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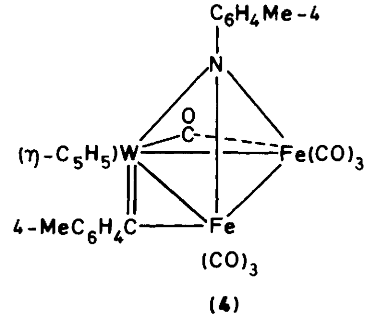

(4)

of the anion $[Ru_3(\mu\text{-}NO)(CO)_{10}]^-$ with CF_3SO_3H in dichloromethane affords the triruthenium compound $[Ru_3(\mu_3\text{-}CO)(\mu_3\text{-}NOH)(CO)_9]$ in which the NOH group caps the metal triangle, as proposed for **(3)**. The ^1H n.m.r. spectra of the latter showed no high-field signal, indicating the absence of a bridging hydrido ligand, as found in $[Ru_3(\mu\text{-}H)(\mu\text{-}NO)(CO)_{10}]$, an isomer of $[Ru_3(\mu_3\text{-}CO)(\mu_3\text{-}NOH)(CO)_9]$ obtained by protonating $[Ru_3(\mu\text{-}NO)(CO)_{10}]^-$ with CF_3CO_2H.[9]

Conclusive evidence for the location of the alkylidyne ligand in **(3)** is provided by the observation in the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of a resonance at 302.1 p.p.m., in the range expected for a $\mu\text{-}CC_6H_4Me\text{-}4$ group bridging the edge of a metal triangle.[2,6,7] In the precursor **(2a)** the signal for $\mu_3\text{-}C$ is seen at 275.6 p.p.m. The ^1H n.m.r. spectrum of **(3)** was also informative. A broad resonance at δ 10.80 is ascribed to the NOH group. In $[Ru_3(\mu_3\text{-}CO)(\mu_3\text{-}NOH)(CO)_9]$ the corresponding n.m.r. peak occurs at δ 8.90.[9] The i.r. spectrum of **(3)** (KBr disc) showed bands in the OH region at 3 379 and 3 370 cm^{-1}. The observation of two absorptions may be due to either a solid-state effect or to isomers. The OH band in the i.r. spectrum of $[Ru_3(\mu_3\text{-}CO)(\mu_3\text{-}NOH)(CO)_9]$[9] appears at 3 495 cm^{-1}.

Formation of the species **(3)** from **(1a)**, *via* the anion **(2a)**, represents a further interesting example of the transformation of a triply-bridging CR group into an edge-bridging μ-CR ligand on a Fe_2W cluster. We referred earlier to the reactions of **(1a)** with sulphur or selenium which gave the complexes $[Fe_2W(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}E)(CO)_7(\eta\text{-}C_5H_5)]$ (E = S or Se), structurally akin to **(3)**. In a further study, we have investigated the reaction between **(1a)** and $MeC_6H_4N_3\text{-}4$. In thf at 60 °C, the product is the red-brown crystalline compound $[Fe_2W(\mu\text{-}CO)(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}NC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)]$ **(4)**. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of **(4)** shows a resonance for the alkylidyne carbon nucleus at δ 303.1 p.p.m., a chemical shift for μ-C very similar to that observed for the edge-bridging carbon nucleus in **(3)**. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of **(4)** also showed signals for Me-4 groups in two different chemical environments, in accord with the structure proposed. The ^1H n.m.r. spectrum was consistent with the $^{13}C\text{-}\{^1H\}$ data. A band at 1 858 cm^{-1} in the i.r. spectrum of **(4)** indicates the presence of a semi-bridging carbonyl group, a common structural feature of clusters of this type. The structure proposed for **(4)** is closely related to that of $[Fe_2W(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}S)(CO)_7(\eta\text{-}C_5H_5)]$, established by *X*-ray diffraction.[3] In the sulphur containing compound the carbonyl group at tungsten semi-bridges the W–Fe vector opposite to the μ-CR-bridged W–Fe bond. The $NC_6H_4Me\text{-}4$ and S groups both serve formally as four-electron donors in these diirontungsten compounds.

Experimental

Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. All solvents were rigorously dried before use. Light petroleum refers to that fraction of b.p. 40—60 °C. The n.m.r. measurements were made with JNM-FX90Q and FX200 instruments. Carbon-13 chemical shifts are positive to high frequency of $SiMe_4$. I.r. spectra were recorded using a Nicolet 10-MX FT spectrophotometer. The compounds $[Fe_2W(\mu_3\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ [R = $C_6H_4Me\text{-}4$ **(1a)**[2] or Me **(1b)**[3]] were prepared as described earlier.

Synthesis of the Salts $[N(PPh_3)_2][Fe_2W(\mu\text{-}CO)(\mu\text{-}NO)(\mu_3\text{-}CR)(CO)_6(\eta\text{-}C_5H_5)]$ (R = Me *or* $C_6H_4Me\text{-}4$).—Both salts were prepared by the same method, so the procedure for **(2b)** is described in detail.

A mixture of the compounds $[Fe_2W(\mu_3\text{-}CMe)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ **(1b)** (0.22 g, 0.34 mmol) and $[N(PPh_3)_2][NO_2]$ (0.20 g, 0.34 mmol) was stirred in thf (15 cm^3) at room temperature for 3 h. The dark red product was filtered through a Celite pad (*ca.* 5 cm), and the solvent was removed *in vacuo*. The residue was dissolved in the minimum amount of thf (*ca.* 2 cm^3), and diethyl ether (*ca.* 6 cm^3) was added slowly to produce red *crystals* of $[N(PPh_3)_2][Fe_2W(\mu\text{-}CO)(\mu\text{-}NO)(\mu_3\text{-}CMe)(CO)_6(\eta\text{-}C_5H_5)]$ **(2b)** (0.26 g, 66%) (Found: C, 51.9; H, 3.2; N, 1.8. $C_{50}H_{38}Fe_2N_2O_8P_2W$ requires C, 52.1; H, 3.3; N, 2.4%); $\nu_{max.}(CO)$ at 2 014m, 1 957s, 1 937s, 1 913m, 1 889m, and 1 797m cm^{-1} (in thf). N.m.r.: ^1H (in CD_2Cl_2), δ 4.29 (s, 3 H, Me), 5.13 (s, 5 H, C_5H_5), and 7.45—7.54 (m, br, 30 H, Ph); $^{13}C\text{-}\{^1H\}$ (in CD_2Cl_2–CH_2Cl_2), δ 277.7 (μ_3-C), 251.8 (WCO), 226.7 (2 FeCO), 218.2 (4 FeCO), 134.1—126.3 (Ph), 88.5 (C_5H_5), and 46.7 p.p.m. (Me).

Dark brown *needles* of $[N(PPh_3)_2][Fe_2W(\mu\text{-}CO)(\mu\text{-}NO)(\mu_3\text{-}CC_6H_4Me\text{-}4)(CO)_6(\eta\text{-}C_5H_5)]\cdot thf$ **(2a)** (0.43 g, 40%) (Found: C, 55.7; H, 4.0; N, 2.2. $C_{56}H_{42}Fe_2N_2O_8P_2W\cdot C_4H_8O$ requires C, 55.4; H, 3.9; N, 2.2%) were obtained from the reaction between **(1a)** (0.62 g, 0.86 mmol) and $[N(PPh_3)_2][NO_2]$ (0.51 g, 0.86 mmol) in thf (15 cm^3). Spectroscopic data for **(2a)**: $\nu_{max.}(CO)$ at 2 017s, 1 963s, 1 945s, 1 913m, 1 884m, and 1 801w cm^{-1} (in thf). N.m.r.: ^1H (in $CDCl_3$), δ 2.26 (s, 3 H, Me-4), 5.12 (s, 5 H, C_5H_5), and 7.40 (m, br, 34 H, C_6H_4 and Ph); $^{13}C\text{-}\{^1H\}$ (in CD_2Cl_2–CH_2Cl_2), δ 275.6 [μ_3-C, *J*(WC) 186 Hz], 246.7 [WCO, *J*(WC) 122 Hz], 225.0 (1 FeCO), 221.1 (2 FeCO), 217.7 (2 FeCO), 214.4 (1 FeCO), 165.0 [$C^1(C_6H_4)$], 134.1—124.6 (C_6H_4 and Ph), 98.5 (C_5H_5), and 21.1 p.p.m. (Me-4).

Protonation Reaction.—A dichloromethane (10 cm^3) solution of **(2a)** (0.40 g, 0.32 mmol) at −50 °C was treated with $HBF_4\cdot Et_2O$ (0.25 mmol). After stirring (30 min), the mixture was allowed to warm to room temperature and passed through alumina (2 × 20 cm). Removal of solvent gave a residue which was crystallised from dichloromethane–light petroleum (5 cm^3, 2:3) to give dark red *crystals* of $[Fe_2W(\mu\text{-}CC_6H_4Me\text{-}4)(\mu_3\text{-}NOH)(CO)_7(\eta\text{-}C_5H_5)]$ **(3)** (0.16 g, 72%) (Found: C, 35.4; H, 2.0; N, 2.1. $C_{20}H_{13}Fe_2NO_8W$ requires C, 34.8; H, 1.9; N, 2.0%); $\nu_{max.}(CO)$ at 2 052s, 2 006vs, 1 984s, 1 961m, 1 940m, and

Table 2. Atomic positional (fractional co-ordinates) parameters (× 10^4), with estimated deviations in parentheses, for the salt (**2a**)

Atom	*x*	*y*	*z*
W	1 827(1)	3 923(1)	853(1)
Fe(1)	1 555(1)	1 979(1)	1 725(1)
Fe(2)	1 554(1)	3 494(1)	2 400(1)
C(1)	2 731(10)	2 840(8)	1 507(6)
C(11)	2 114(14)	5 550(7)	64(8)
C(12)	3 159	5 064	207
C(13)	3 581	4 135	−135
C(14)	2 796	4 046	−490
C(15)	1 890	4 921	−367
C(21)	3 983(5)	2 510(6)	1 372(4)
C(22)	4 610	3 203	1 426
C(23)	5 774	2 885	1 322
C(24)	6 311	1 873	1 164
C(25)	5 683	1 180	1 110
C(26)	4 520	1 498	1 214
C(27)	7 620(10)	1 485(13)	1 103(8)
N(1)	642(10)	4 677(9)	1 603(7)
O(1)	−151(8)	5 373(7)	1 837(6)
C(2)	1 829(12)	4 657(12)	2 558(9)
O(2)	2 001(11)	5 410(11)	2 666(8)
C(3)	2 325(13)	2 774(14)	3 023(9)
O(3)	2 857(10)	2 354(13)	3 447(7)
C(4)	136(12)	3 404(11)	3 059(8)
O(4)	−760(8)	3 319(9)	3 518(6)
C(5)	776(10)	3 173(8)	824(7)
O(5)	62(9)	2 951(8)	631(7)
C(6)	2 142(11)	1 016(11)	2 366(9)
O(6)	2 547(10)	374(9)	2 773(7)
C(7)	2 055(10)	1 229(9)	971(9)
O(7)	2 379(8)	768(7)	450(6)
C(8)	110(11)	1 807(10)	2 198(8)
O(8)	−817(7)	1 628(7)	2 517(7)
P(1)	−5 431(2)	3 005(2)	7 189(2)
P(2)	−7 229(2)	2 037(2)	7 079(2)
N	−6 486(7)	2 442(7)	7 445(5)
C(111)	−4 689(6)	2 458(6)	7 891(4)
C(112)	−5 205	1 834	8 593
C(113)	−4 657	1 463	9 159
C(114)	−3 594	1 716	9 023
C(115)	−3 078	2 340	8 320
C(116)	−3 625	2 711	7 754
C(121)	−5 877(6)	4 399(4)	7 199(4)
C(122)	−7 039	4 818	7 419
C(123)	−7 401	5 895	7 450
C(124)	−6 600	6 552	7 260
C(125)	−5 438	6 133	7 039
C(126)	−5 076	5 056	7 009
C(131)	−4 410(6)	2 816(5)	6 250(3)
C(132)	−3 737	1 820	6 173
C(133)	−3 000	1 619	5 440
C(134)	−2 936	2 412	4 784
C(135)	−3 609	3 408	4 862
C(136)	−4 346	3 609	5 595
C(211)	−8 461(6)	1 680(6)	7 852(4)
C(212)	−9 111	1 063	7 735
C(213)	−10 052	740	8 345
C(214)	−10 342	1 035	9 073
C(215)	−9 691	1 653	9 191
C(216)	−8 750	1 975	8 581
C(221)	−7 651(7)	2 986(5)	6 323(4)
C(222)	−8 721	3 631	6 494
C(223)	−9 016	4 412	5 911
C(224)	−8 241	4 548	5 157
C(225)	−7 170	3 903	4 985
C(226)	−6 875	3 122	5 568
C(231)	−6 499(6)	866(5)	6 682(4)
C(232)	−5 733	182	7 035
C(233)	−5 169	−770	6 773
C(234)	−5 369	−1 039	6 159
C(235)	−6 135	−356	5 805
C(236)	−6 700	597	6 067
C(31)	−818(21)	8 570(30)	5 015(12)
C(32)	−51	7 648	4 774
C(33)	614	7 922	3 981
C(34)	258	9 014	3 732
O(35)	−627	9 414	4 371

1 857w br cm^{-1} (in CH_2Cl_2); $\nu_{max.}$(OH) at 3 379 and 3 370 cm^{-1} (KBr disc). N.m.r.: ^1H (in CD_2Cl_2), δ 2.26 (s, 3 H, Me-4), 5.90 (s, 5 H, C_5H_5), 7.12—7.40 (m, br, 4 H, C_6H_4), and 10.80 (br 1 H, OH); ^{13}C-{^1H} (in CD_2Cl_2–CH_2Cl_2), δ 302.1 (μ-C), 240.9 (WCO), 212.8, 209.9 (FeCO), 152.5 [$C^1(C_6H_4)$], 139.5, 130.5, 129.9 (C_6H_4), 97.5 (C_5H_5), and 21.8 p.p.m. (Me-4).

Reaction between [$Fe_2W(\mu_3$-CC_6H_4Me-4)(μ-CO)$(CO)_8$(η-C_5H_5)] *and* $MeC_6H_4N_3$-4.—A mixture of (**1a**) (0.49 g, 0.68 mmol) and $MeC_6H_4N_3$-4 (0.68 mmol) was heated in thf (35 cm^3) at 60 °C for 6 h. After cooling to room temperature, solvent was removed *in vacuo*, and the residue dissolved in light petroleum–dichloromethane (10 cm^3, 1:1) and chromatographed on a Florisil column (2 × 20 cm). Elution with the same solvent mixture gave a dark brown solution. Evaporation of the latter and crystallisation from light petroleum–dichloromethane (4:1) afforded dark red-brown *crystals* of [Fe_2W(μ-CO)(μ-CC_6H_4Me-4)(μ_3-NC_6H_4Me-4)$(CO)_6$(η-C_5H_5)] (**4**) (0.21 g, 40%) (Found: C, 40.7; H, 2.6; N, 1.4. $C_{27}H_{19}Fe_2NO_7W$ requires C, 42.4; H, 2.6; N, 1.8%); $\nu_{max.}$(CO) at 2 052s, 2 008vs, 1 981m, 1 962m, 1 942m, and 1 858w br cm^{-1} (in CH_2Cl_2). N.m.r.: ^1H (in CD_2Cl_2), δ 2.28 (s, 3 H, Me-4), 2.38 (s, 3 H, Me-4), 5.57 (s, 5 H, C_5H_5), 7.08—7.42 (m, br, 8 H, C_6H_4); ^{13}C-{^1H} (in CD_2Cl_2–CH_2Cl_2), δ 303.1 (μ-C), 240.3 (WCO), 215.5, 213.3, 207.7 (FeCO), 167.3, 152.4 [$C^1(C_6H_4)$], 139.6—127.1 (C_6H_4), 99.8 (C_5H_5), 21.9, and 21.0 p.p.m. (Me-4).

Crystal Structure Determination of [$N(PPh_3)_2$][Fe_2W(μ-CO)(μ-NO)(μ_3-CC_6H_4Me-4)$(CO)_6$(η-C_5H_5)]·thf (**2a**).—Crystals of (**2a**) were grown from thf–diethyl ether as dark red prisms. Diffracted intensities were collected at room temperature from a crystal of dimensions *ca.* 0.6 × 0.3 × 0.2 mm. Data were collected (ω scans) on a Nicolet $P2_1$ four-circle diffractometer. Of the total 5 660 intensities collected to $2\theta \leqslant 40°$, 4 095 had $F \geqslant 5.0\sigma(F)$, where $\sigma(F)$ is the standard deviation based on counting statistics, and only these were used in the solution and refinement of the structure, after the data had been corrected for Lorentz and polarisation effects. An absorption correction was not applied.

Crystal data for (**2a**). $C_{56}H_{42}Fe_2N_2O_8P_2W{\cdot}C_4H_8O$, M = 1 300.6, triclinic, a = 12.744(4), b = 13.224(4), c = 18.582(6) Å, α = 76.06(2), β = 69.01(2), γ = 75.99(2)°, U = 2 796(1) Å^3, Z = 2, D_c = 1.55 g cm^{-3}, $F(000)$ = 1.384, space group $P\bar{1}$, Mo-K_α *X*-radiation (graphite monochromator, $\bar{\lambda}$ = 0.710 69 Å), μ(Mo-K_α) = 27.21 cm^{-1}.

The structure was solved, and all non-hydrogen atoms were located, by conventional heavy-atom and difference-Fourier methods. The spectroscopic data for (**2a**) indicate that the tungsten atom is bonded to a semi-bridging carbonyl group. However, the *X*-ray data do not unambiguously distinguish between this ligand and the NO group, but the choice adopted gave sensible W–CO and W–NO separations and a marginal improvement in the refinement. However, the possibility that these ligands are in fact disordered in the solid-state structure cannot be ruled out. Hydrogen atoms were not included in the refinement, and all atoms in the anion were given anisotropic thermal parameters. For the $[N(PPh_3)_2]^+$ cation the phosphorus and nitrogen atoms were given anisotropic thermal parameters and the phenyl rings were treated as rigid isotropic groups. The cyclopentadienyl and tolyl ring systems were also treated as rigid groups. The complex crystallises with one disordered molecule of thf in the asymmetric unit. This was approximated in the refinement to a rigid, planar five-membered ring with correspondingly large anisotropic thermal parameters for the constituent atoms. Refinement by block-cascade least squares led to R 0.049 (R' 0.052), and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.001|F|^2]$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks $\geqslant 0.7$ e Å^{-3}. Scattering factors were from ref. 10. All computations were carried out on an Eclipse (Data General) computer with the SHELXTL system of programs.[11] Atom co-ordinates are listed in Table 2.

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References

1 Part 41, M. Green, J. A. K. Howard, A. P. James, C. M. Nunn, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1986, 187.
2 L. Busetto, J. C. Jeffery, R. M. Mills, F. G. A. Stone, M. J. Went, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 101.
3 E. Delgado, A. T. Emo, J. C. Jeffery, N. D. Simmons, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1985, 1323.
4 J. C. Jeffery, K. A. Mead, H. Razay, F. G. A. Stone, M. J. Went, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1984, 1383.
5 R. E. Stevens and W. L. Gladfelter, *Inorg. Chem.*, 1983, **22**, 2034; W. L. Gladfelter, *Adv. Organomet. Chem.*, 1985, **24**, 41.
6 G. A. Carriedo, J. C. Jeffery, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1984, 1597.
7 J. A. Abad, L. W. Bateman, J. C. Jeffery, K. A. Mead, H. Razay, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 2075.
8 H. B. Chin, M. B. Smith, R. D. Wilson, and R. Bau, *J. Am. Chem. Soc.*, 1974, **96**, 5285; R. D. Wilson and R. Bau, *ibid.*, p. 7601; L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1981, 1134 and refs. therein.
9 R. E. Stevens and W. L. Gladfelter, *J. Am. Chem. Soc.*, 1982, **104**, 6455.
10 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
11 G. M. Sheldrick, SHELXTL programs for use with the Nicolet *P*3*m* *X*-ray system, University of Cambridge, 1976; updated Göttingen, 1982.

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