Reaction of $[WMe(CO)_3(\eta-C_5H_5)]$ with $LiBHEt_3$. Formation and Reactions of the Anionic Formyl *trans*-$[W(CHO)Me(CO)_2(\eta-C_5H_5)]^-$ and the Anionic Hydrido Acyl *trans*-$[WH(COMe)(CO)_2(\eta-C_5H_5)]^-$

J. Trevor Gauntlett, Brian E. Mann, Mark J. Winter* and Simon Woodward
Department of Chemistry, The University, Sheffield S3 7HF, UK

Addition of $LiBHEt_3$ to $[WMe(CO)_3(\eta-C_5H_5)]$ **5** at −70 °C results in the formation of the formyl *trans*-$[W(CHO)Me(CO)_2(\eta-C_5H_5)]^-$ **7**. In solution, this species exists as a mixture of two BEt_3 adducts and a BEt_3-free species. All the formyl species undergo chemical exchange at −50 °C. Warming of the reaction mixture to ambient temperature results in solutions containing the anionic hydrido acyl complex *trans*-$[WH(COMe)(CO)_2(\eta-C_5H_5)]^-$ **6** isolable as a boron-free salt $[Li(12\text{-crown-}4)_2][WH(COMe)(CO)_2(\eta-C_5H_5)]$ (12-crown-4 = 1,4,7,10-tetraoxacyclododecane). This moisture-sensitive anion gives $[W(CO)_3(\eta-C_5H_5)]^-$ on exposure to water and undergoes hydride for halide (X) exchange on low-temperature treatment with CCl_4, CBr_4 or CHI_3 forming the reactive anions $[WX(COMe)(CO)_2(\eta-C_5H_5)]^-$ **8**–**10**. The major product of warming these halogenoacyl anions is **5**. Addition of $[Me_3O][BF_4]$ to boron-free solutions of $[WI(COMe)(CO)_2(\eta-C_5H_5)]^-$ **10** results in the new carbene *trans*-$[WI\{=C(OMe)Me\}(CO)_2(\eta-C_5H_5)]$ **11**, while treatment with $SiMe_3Cl$ followed by low-temperature filtration through silica gives the hydroxycarbene *trans*-$[WI\{=C(OH)Me\}(CO)_2(\eta-C_5H_5)]$ **12**.

The interesting feature of many reactions between metal carbonyl derivatives and sources of hydride is that the initial products are frequently formyl complexes $[M(CHO)L_n]$,[1] such as $[Cr(CHO)(CO)_2\{P(OMe)_3\}(\eta-C_5Me_5)]$,[2] $[Re(CHO)(PPh_3)(NO)(\eta-C_5H_5)]$,[3] and $[Re_2(CHO)(CO)_9]^-$.[4] Such complexes are important, in part, because of the relevance of formyls to CO reduction chemistry.[5] One hydride source that has attracted particular attention is $LiBHEt_3$.[6] One of its advantages is that after functioning as a source of hydride the only by-product is BEt_3. In principle, this should be easily removable from the reaction mixture since it is volatile.

We reported previously[7] the reaction of $[MoMe(CO)_3(\eta-C_5H_5)]$ **1** with $LiBHEt_3$. The eventual result is the formation of an anionic acetaldehyde complex $[Mo(CO)_2(MeCHO)(\eta-C_5H_5)]^-$ **2** (Scheme 1). The two characterized intermediates are the formyl $[Mo(CHO)Me(CO)_2(\eta-C_5H_5)]^-$ **3** and the hydrido acyl $[MoH(COMe)(CO)_2(\eta-C_5H_5)]^-$ **4**. Since we required to establish the generality or otherwise of such reactions, we examined the analogous tungsten systems and therefore in this paper we report some observations on the reaction of $[WMe(CO)_3(\eta-C_5H_5)]$ **5** with $LiBHEt_3$. Some aspects of this work are the subject of a preliminary communication.[8]

Results and Discussion

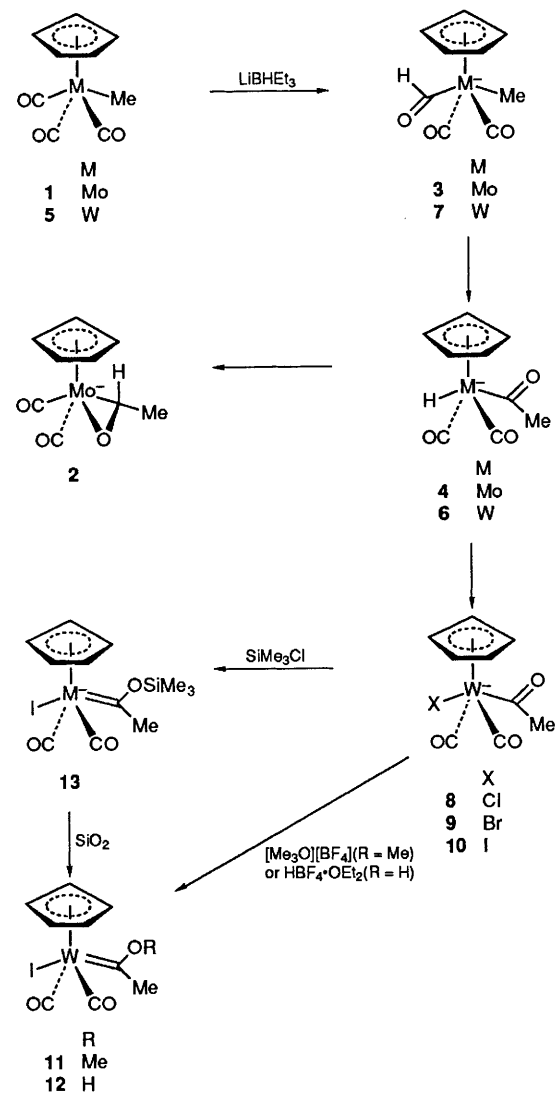
The reaction between $LiBHEt_3$ and $[WMe(CO)_3(\eta-C_5H_5)]$ **5** in tetrahydrofuran (thf) solution proceeds at ambient temperature to form a single product identified as the anionic hydrido acyl $[WH(COMe)(CO)_2(\eta-C_5H_5)]^-$ **6** (Scheme 1). If the reaction is carried out at −70 °C, and the mixture warmed towards ambient temperature, a single intermediate is observable in the reaction mixture (IR and NMR spectra). This is the formyl $[W(CHO)Me(CO)_2(\eta-C_5H_5)]^-$ **7**.

The Formyl $[W(CHO)Me(CO)_2(\eta-C_5H_5)]^-$ **7**.—Addition of $LiBHEt_3$ to a solution in thf of the tricarbonyl **5** at −70 °C leads to a single anionic dicarbonyl [ν_{CO}(thf, −70 °C): 1917m and 1826s cm^{-1}]. The relative intensities of the carbonyl stretching bands are those of a single *trans* dicarbonyl.[9] However, subtleties are revealed on monitoring the reaction by ^1H and ^{13}C NMR spectroscopy.

As the $LiBHEt_3$ is supplied in undeuteriated thf, and BEt_3 by-products are produced in the reaction, useful ^1H NMR data are found only in those regions where thf and BEt_3 do not give signals. Reproducible spectra obtained by low-temperature mixing of $[WMe(CO)_3(\eta-C_5H_5)]$ **5** and $LiBHEt_3$ show three high-frequency signals (Fig. 1). Such signals are indicative of metal formyl complexes.

Only one cyclopentadienyl resonance is observed [δ_H(thf, −70 °C): 5.05], while the methyl signal is obscured by BEt_3 resonances. The intensity ratio of the two outer formyl signals at δ_H 14.68 and 12.18 is constant in a number of experiments, while the strength of the central signal varies, depending on reactant concentrations and the batch of $LiBHEt_3$. Addition of a solution of BEt_3 in thf to the reaction mixture at −60 °C causes the central resonance at δ_H 14.00 to disappear. Spin-saturation transfer experiments at −50 °C show that all three formyl complexes undergo chemical exchange. Reinforcing this, the formyl signals also show a temperature-dependent reversible broadening (Fig. 1). Unfortunately lower temperature data acquisitions are not attainable owing to increasing viscosity in thf around −80 °C.

These observations are interpreted as follows. Hydride attack by $LiBHEt_3$ on the alkyl **5** gives the formyl **7** and BEt_3. Complexation of the evolved BEt_3 at the formyl oxygen of some **7** (represented by the central ^1H NMR signal) gives two isomeric adducts with BEt_3, **7**·BEt_3, represented by the two outer signals in the ^1H NMR spectra. Addition of extra BEt_3 to the reaction solution complexes out the remaining **7** as **7**·BEt_3. It is quite probable that the formyl group in uncomplexed **7** rotates very freely between the two forms **7a** and **7b** related by formyl orientation as indicated in Scheme 2. This motion is not frozen out at −70 °C in the ^1H NMR spectrum, although the signal is quite broad. However the spectra do not exclude the possibility that the formyl exists as just one of either **7a** or **7b**.



Scheme 1

Slow interconversion of all **7** and **7**•BEt_3 occurs at low temperature. There are at least two explanations for the two outer formyl signals. Neglecting steric preferences, the two signals assigned to **7**•BEt_3 can be a consequence of the slow interconversion of **7a**•BEt_3 with **7b**•BEt_3 or **7a′**•BEt_3 with **7b′**•BEt_3 (rotation about the tungsten–formyl bond, fast interconversion of **7a**•BEt_3 with **7a′**•BEt_3 and **7b**•BEt_3 with **7b′**•BEt_3). The other possibility is the slow interconversion of **7a**•BEt_3 with **7a′**•BEt_3 or **7b**•BEt_3 with **7b′**•BEt_3 (BEt_3–oxygen lone pair site interconversion, fast interconversion of **7a**•BEt_3 with **7b**•BEt_3 and **7a′**•BEt_3 with **7b′**•BEt_3). It is not possible to distinguish these pairs of possibilities on the NMR evidence available.

One would expect that the concentration of species such as **7b**•BEt_3 would be low for steric reasons (clash of BEt_3 with cyclopentadienyl). This would mean that the tungsten–formyl rotation path would principally involve interconversion of **7a′**•BEt_3 with **7b′**•BEt_3 (fast **7a**•BEt_3–**7a′**•BEt_3 interconversion) while the BEt_3–oxygen lone pair site interconversion pathway would involve slow interconversion of **7a**•BEt_3 with **7a′**•BEt_3 (fast **7a′**•BEt_3–**7b′**•BEt_3 interconversion).

The above conclusions are reinforced by the ^{13}C NMR spectra. After initial mixing, the ^{13}C NMR spectrum at −50 °C shows three cyclopentadienyl, three methyl and three carbonyl resonances. These signals are in addition to minor peaks assigned to traces of starting material **5** {δ_C[$^2H_8$]thf, −50 °C): 93.4 (η-C_5H_5), −34.0 (Me)} and $[W(CO)_3(\eta\text{-}C_5H_5)]^-$ [δ 88.8 (η-C_5H_5)]. These are assigned to **7**, **7a**•BEt_3 and **7b**•BEt_3. These results back up the conclusions of the ^1H NMR experiments. Only two formyl signals are apparent, but probably two signals overlap at δ 268.5. Given the similar nature of

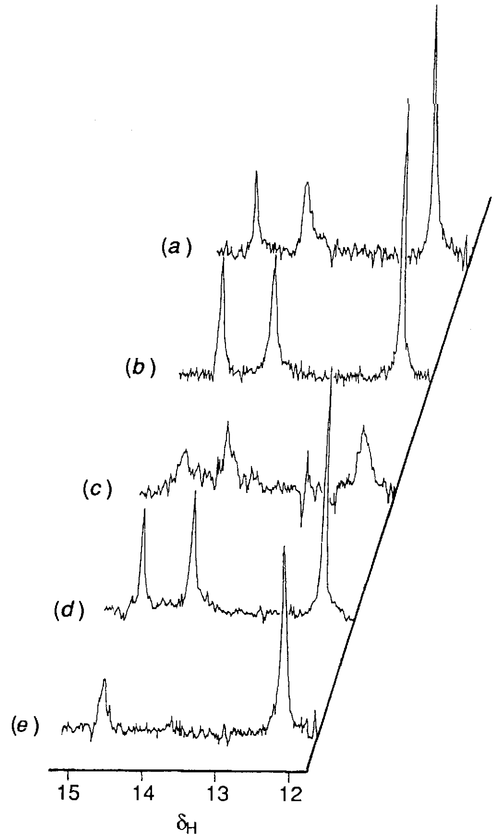
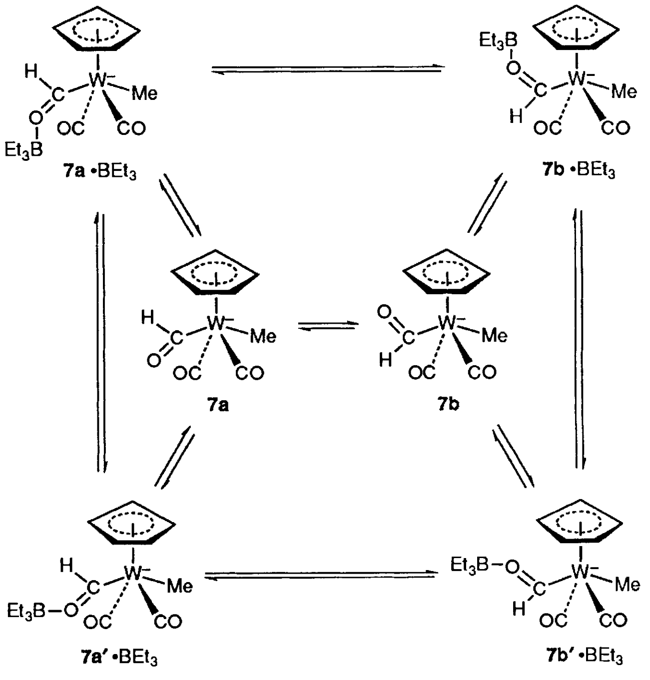


Fig. 1 Proton NMR spectrum of $[W(CHO)Me(CO)_2(\eta\text{-}C_5H_5)]^-$ **7** in the formyl region. Conditions: (*a*) immediately after mixing reagents at −70 °C, (*b*) warming to −50 °C, (*c*) warming to −30 °C, (*d*) recooling to −50 °C and (*e*) after addition of BEt_3 at −60 °C, spectrum recorded at −60 °C



Scheme 2

the complexes, such an overlap, while unfortunate, is not unlikely.

The presence of just two carbonyl stretches in the low-temperature IR spectrum is a consequence of overlapping signals for all the formyl rotamers. They overlap because of the broad nature of carbonyl IR spectra in thf and the very small effect the formyl orientation and BEt_3 complexation are expected to have on ν_{CO}.

The reaction of $LiBHEt_3$ with metal carbonyls is a recognized general route to metal formyls.[1] However, little is written concerning the fate of the BEt_3 by-product. Formyl chemical shifts of complexes generated in this way are often dependent on BEt_3 concentration.[1] While such effects are frequently attributed to exchange processes such as in Scheme 2, direct observation of formyl adducts is rare. Surprisingly, there is no indication of BEt_3 adduct formation by the analogous molybdenum formyl *trans*-$[Mo(CHO)Me(CO)_2(\eta\text{-}C_5H_5)]^-$, **3**.[7] The neutral formyls *cis*- and *trans*-$[M(CHO)(CO)_2(PR_3)(\eta\text{-}C_5Me_5)]$ (M = Cr or Mo; R = Ph or OMe) are known, but, again, there is no suggestion of adduct formation.[2,10] There are a few reports of formyl boron adducts.[11,12] For instance, $NaBH_4$ reduction of $[Fe(CO)_2(PMe_3)(\eta\text{-}C_5Me_5)]^+$ results in BH_3 adducts of $[Fe(CHO)(CO)(PMe_3)(\eta\text{-}C_5Me_5)]$ in which it is felt that the $C(O\cdot BH_3)H$ formyl unit undergoes facile iron–formyl bond rotation.[12] On the other hand, it is suggested that the NMR spectra of BF_3 adducts of cycloalkanones are interpreted by a process involving BF_3 exchange between the two sp^2 oxygen lone pair orbitals.[13]

Storage of concentrated solutions (*ca.* 150 mg cm^{-3}) of the formyl **7** at −70 °C results in precipitation of a yellow powder. Removal of thf, washing with pentane, and pumping under vacuum at −35 °C gives a yellow powder, the $[Li(thf)_n]^+$ salt of **7**. Removal of solvents is slow at −35 °C and traces still remain after 4 h under vacuum. Warming to −10 °C while pumping removes the last of the pentane, but at this temperature the yellow powder converts to an oil, which then solidifies to a yellow solid. The solid-state IR spectrum of this solid (KBr disc) is identical to that of the $[Li(thf)_n]^+$ salt of **6** (see below), indicating isomerization of the formyl **7**. Warming thf solutions of the formyl **7** above −20 °C also results in rearrangement to the anionic hydrido acyl *trans*-$[WH(COMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ **6** (Scheme 2). As a consequence of these properties of **7**, no elemental analysis was obtained.

The Hydrido Acyl trans-$[WH(COMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ **6**.—The isomerization of the formyl **7** into the hydrido acyl complex **6** is conveniently followed by variable-temperature IR spectroscopy. An identical solution is generated if the $LiBHEt_3$ is added to the alkyl **5** at room temperature, although in this case no intermediate is observed due to the rapidity of the reaction.

The ^1H NMR spectrum of the reaction mixture shows single product cyclopentadienyl and methyl resonances [δ_H(thf): 4.94 (s, 5 H, $\eta\text{-}C_5H_5$) and 2.25 (s, 3 H, Me)] together with a clear hydride signal (δ_H −6.18) which has ^{183}W satellites. Signals attributed to BEt_3 are also observed, together with a small peak whose variation with temperature confirms it to be $[Et_3B\text{–}H\text{–}BEt_3]^-$.[14] Given the slight excess of $LiBHEt_3$ used during the formation of **6**, its presence is not unexpected. The IR spectrum of **6** is characteristic of an anionic *trans* dicarbonyl and this is reinforced by the ^{13}C NMR spectrum, which shows a very high frequency acyl signal [δ_C(thf-[$^2H_8$]toluene): 286.4] and just a single CO resonance in addition to cyclopentadienyl and methyl signals.

Isolation of **6** as its $[Li(thf)_n]^+$ salt is achieved by removal of the thf solvent under vacuum followed by washing with light petroleum. This yields a bright yellow highly reactive solid, apparently $[Li(thf)_n][WH\{C(O\cdot BEt_3)Me\}(CO)_2(\eta\text{-}C_5H_5)]$ (n = 3–4). The proton NMR signals of this material are broad in CD_2Cl_2 both at ambient temperature and at −50 °C, but integrations show one mole of BEt_3 per mole of **6**. Satisfactory ^{13}C NMR spectra could not be obtained on this material in CD_2Cl_2.

Addition of 1,4,7,10-tetraoxacyclododecane (12-crown-4) to the reaction mixture containing **6** causes no change in the IR spectrum, implying that **6** exists as solvent separated ion pairs in solution whereas changes in the carbonyl spectrum would have suggested that the lithium cation is bound to **6**, probably by an isocarbonyl interaction. Removal of the thf and washing with Et_2O gives a pale yellow powder, the $[Li(12\text{-crown-}4)_2]^+$ salt of **6** in good yield (78%). Alternatively, addition of $LiBHEt_3$ to the alkyl **5** dissolved in Et_2O in the presence of 12-crown-4 causes the immediate precipitation of the same salt in similar yield. This latter preparation is more convenient. Reproducible ^1H NMR spectra indicate that this salt *does not* contain BEt_3, and that there are *two* crown ether molecules per lithium cation. A very clear low-frequency hydride signal displays ^{183}W satellites [$\delta(CD_2Cl_2)$: −6.22 (s, 1 H, WH, $^1J_{WH}$ 46 Hz)]. It is relatively unusual for two 12-crown-4 ligands to associate with a lithium cation but a number of other examples are characterized crystallographically.[15] Unfortunately, the poor crystallinity of $[Li(12\text{-crown-}4)_2][WH(COMe)(CO)_2(\eta\text{-}C_5H_5)]$ prevented an X-ray crystallographic study.

Apart from the differences due to the 12-crown-4 and lack of BEt_3, the ^1H and ^{13}C NMR spectra (Table 1) of isolated $[Li(12\text{-crown-}4)_2][WH(COMe)(CO)_2(\eta\text{-}C_5H_5)]$ are very similar to those of the reaction mixture and require little further comment. The negative-ion FAB mass spectrum confirms the relative molecular mass of the anion as 349. Satisfactory elemental analyses could not be obtained on samples of $[Li(12\text{-crown-}4)_2][WH(COMe)(CO)_2(\eta\text{-}C_5H_5)]$ due to its rapid decomposition in air.

Often, the reactivity of $[Li(thf)_n]$ $[WH(COMe)(CO)_2(\eta\text{-}C_5H_5)]$ produced *in situ* (and therefore containing BEt_3) is very similar to that of the $[Li(12\text{-crown-}4)_2]^+$ salt, meaning that it is frequently not necessary to isolate the anion before further reaction. In whatever form handled, **6** is very moisture-sensitive. The consequence of water contamination or addition is the formation of $Li[W(CO)_3(\eta\text{-}C_5H_5)]$ [$\delta_H(CD_2Cl_2)$: 5.16 (s, 5 H, $\eta\text{-}C_5H_5$)]. Methane is evolved in the reaction and detected by GLC.

Hydrido acyl complexes are a rare class of compounds. Although accepted as intermediate in, for example, hydroformylation[5] and aldehyde decarbonylation reactions,[16] only a few examples have been isolated. A short report describes the preparations of *cis*-$[ReH(COMe)(CO)_4]^-$ by the reaction of LiMe with $[ReH(CO)_5]$ or by treatment of $[Re(COMe)(CO)_5]$ with $LiBHEt_3$ followed by gentle warming at 32 °C.[17] Other hydrido acyl complexes are generated by oxidative addition of aldehydes to co-ordinatively unsaturated metal complexes.[18]

Reactions of $[WH(COMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ **6**.—The molybdenum analogue of **6**, *trans*-$[MoH(COMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ **4**, undergoes rearrangement below 0 °C to give the aldehyde complex *cis*-$[Mo(CO)_2(MeCHO)(\eta\text{-}C_5H_5)]^-$ **2**.[7] The tungsten hydrido acyl **6** shows no signs of converting to the hypothetical *cis*-$[W(CO)_2(MeCHO)(\eta\text{-}C_5H_5)]^-$. Perhaps the formation of the tungsten–aldehyde linkage would not compensate thermodynamically for the loss of the W–H bond, expected to be stronger in **6** than in the molybdenum species **4**.

The hydridoacyl **6** does demonstrate other reactions however. Anionic acyls such as $[W(COPh)(CO)_5]^-$ are good sources of Fischer carbenes on reaction with alkylating agents.[19] A similar reactivity for **6** on reaction with such reagents would lead to hydrido carbenes of the type $[WH\{{=}CMe(OR)\}(CO)_2(\eta\text{-}C_5H_5)]$.

In fact, addition of $[Me_3O][BF_4]$ to reaction mixtures containing $[Li(thf)_n]$ $[WH(COMe)(CO)_2(\eta\text{-}C_5H_5)]$ leads only to the regeneration of **5**. Attempted methylation of the $[Li(12\text{-crown-}4)_2]^+$ analogue leads to a mixture of some **5** and other very unstable, uncharacterized *cis* and *trans* dicarbonyls. The

Table 1 IR, ^{1}H and ^{13}C NMR spectroscopic data for the complexes[a]

Compound	ν_{CO}/cm^{-1}	δ_H	δ_C
6[b]	1907m, 1816s	4.94 (s, 5 H, η-C_5H_5), 2.25 (s, 3 H, Me), −6.18 (s, 1 H, WH, $^1J_{WH}$ 44.5 Hz)	286.4 (*C*OMe), 229.8 (CO), 89.8 (η-C_5H_5), 54.5 (Me)[c]
6[d]	1902m, 1803s[e]	5.10 (s, 5 H, η-C_5H_5), 3.75 (s, 32 H, OCH_2), 2.31 (s, 3 H, Me), −6.22 (s, 1 H, WH, $^1J_{WH}$ 46 Hz)[f]	295.2 (*C*OMe), 230.0 (CO), 90.9 (η-C_5H_5), 70.2 (OCH_2), 54.6 (Me)[g]
7	1917m, 1826s[h]	14.68, 14.00, 12.18 (formyls, see text), 5.05 (s, 5 H, Me)[i]	276.9, 268.5 (CHO); 227.3, 225.1, 221.4 (CO); 95.0, 93.2, 92.8 (η-C_5H_5); −29.8, −30.0, −31.4 (Me)
8	1945m, 1846s	5.05 (s, 5 H, η-C_5H_5), 2.60 (s, 3 H, Me)	
9	1943m, 1845s	4.95 (s, 5 H, η-C_5H_5), 2.48 (s, 3 H, Me)	
10	1937m, 1846s	5.01 (s, 5 H, η-C_5H_5), 2.47 (s, 3 H, Me)	
11	1979m, 1897s[e]	5.64 (s, 5 H, η-C_5H_5), 3.94 (s, 3 H, OMe), 2.93 (s, 3 H, Me)[j]	299.8 (W=C), 218.4 (CO), 96.2 (η-C_5H_5), 60.5 (OMe), 44.9 (Me)[k]
12	1976m, 1898s	12.65 (s, br, 1 H, OH), 5.65 (s, 5 H, η-C_5H_5), 2.61 (s, 3 H, Me)	295.6 (W=C), 218.1 (CO), 94.4 (η-C_5H_5), 47.2 (Me)[k]

[a] In thf or thf–[$^2H_8$]thf unless specified. [b] As $[Li(thf)_n]^+$ salt. [c] In thf–[$^2H_8$]toluene. [d] As $[Li(12\text{-crown-}4)_2]^+$ salt. [e] In CH_2Cl_2. [f] In CD_2Cl_2. [g] In CD_3OD at −50 °C. [h] At −50 °C. [i] See Fig. 1, methyl signals obscured by BEt_3 signals. [j] In $CDCl_3$. [k] In [$^2H_6$]acetone at −50 °C.

alkyl **5** is regenerated by hydride abstraction from **6**, followed by retro alkyl insertion of the resulting intermediate [W(COMe)(CO)$_2$(η-C$_5$H$_5$)] (or its solvate).

One way to prevent hydride abstraction is, of course, to replace the hydride before alkylation. This is accomplished by the addition of CCl$_4$, CBr$_4$ or CHI$_3$ at −80 °C to freshly generated solutions of **6**, followed by warming towards ambient temperature. The result is hydride for halide exchange resulting in anionic halogenoacyls [WX(COMe)(CO)$_2$(η-C$_5$H$_5$)]$^-$ (X = Cl, **8**; Br, **9**; or I, **10**). This type of behaviour is quite well known for mononuclear hydride complexes and often serves to demonstrate the presence of labile hydride complexes.[20]

Provided that the spectra are run quickly, it is possible to obtain ^{1}H NMR and IR data on these anionic acyls. The ^{1}H NMR spectrum after addition of CHI$_3$ to a solution of **6** shows four new signals associated with organotransition metal species. Two of these are associated with **10** [δ_H([^{2}H$_8$]thf): 5.01 (s, 5 H, η-C$_5$H$_5$) and 2.47 (s, 3 H, COMe)] and two with **5** [δ_H([^{2}H$_8$]thf): 5.51 (s, 5 H, η-C$_5$H$_5$) and 0.35 (s, 3 H, Me)]. A further singlet at δ_H 3.94 is assigned to CH$_2$I$_2$ and this is confirmed by spectra of authentic samples. The signals attributed to **5** grow in with time, replacing those due to **10**. Rapidly recorded IR spectra of the reaction mixture indicate the anionic dicarbonyl **10** [ν_{CO}(thf): 1937m and 1846s cm^{-1}] which converts to the neutral tricarbonyl **5** [ν_{CO}(thf): 2013s and 1917s cm^{-1}]. Clearly, the anion **10** loses I$^-$ at ambient temperature and rearranges by a retro migratory insertion reaction to **5**. It is worth noting that [MoMe(CO)$_3$(η-C$_5$H$_5$)] does not react with I$^-$ under a number of different conditions and the tendency of **10** to iodide loss fits in with that result. The corresponding halides **8** and **9** are similarly characterized, although they are much less stable. Consequently, all subsequent preparations involving these halogeno acyl anions were performed with **10**. In the cases where the anions **8**–**10** are produced in the presence of BEt$_3$, it is not clear whether these anions are associated with BEt$_3$ in solution. However, iodide for hydride exchange is also accomplished by treating [Li(12-crown-4)$_2$][WH(COMe)(CO)$_2$(η-C$_5$H$_5$)] with CHI$_3$, in which case there is definitely no BEt$_3$ associated with the anion **10**. The reactivity of **10** does vary according to whether BEt$_3$ is present in the solution.

Addition of [Me$_3$O][BF$_4$] to a solution of **10** generated from [Li(12-crown-4)$_2$][WH(COMe)(CO)$_2$(η-C$_5$H$_5$)] gives three products which are separable by chromatography. These are the starting material **5**, traces of [WI(CO)$_3$(η-C$_5$H$_5$)], and the new carbene complex *trans*-[WI{=C(OMe)Me}(CO)$_2$(η-C$_5$H$_5$)] **11** in low and variable isolated yields up to 22%. The spectroscopic properties of this compound are clearly closely related to those of the known cyclic carbene complex *trans*-[WI{=C(CH$_2$)$_3$O}(CO)$_2$(η-C$_5$H$_5$) and require no comment.[21] This alkylation reaction is clearly related to known syntheses of *cis*- and *trans*-[W(CN){=CMe(OR)}(CO)$_2$(η-C$_5$H$_5$)] by addition of [R$_3$O][BF$_4$] (R = Me or Et) to *cis*- and *trans*-[W(CN)(COMe)(CO)$_2$(η-C$_5$H$_5$)]$^-$.[22] The reason for the low and variable isolated yields of **11** is that as **10** is being formed it converts to **5**, and this competes with the alkylation step. This competition will depend on precise instantaneous concentrations of reagents and temperatures. If BEt$_3$ is present during the alkylation step, as when **6** is prepared *in situ*, the only isolated products are **5** and [WI(CO)$_3$(η-C$_5$H$_5$)]. The reason for the differing reactivity may be linked to co-ordination of BEt$_3$ at the acyl of **10** in such solutions and so blocking that alkylation site.

One might expect that the carbene **11** would also form on addition of LiMe to [WI(CO)$_3$(η-C$_5$H$_5$)] (which should give **10**), followed by alkylation with [Me$_3$O][BF$_4$]. This does not happen. Instead, formation of [W(CO)$_3$(η-C$_5$H$_5$)]$^-$ and some **5** is observed.

Addition of HBF$_4$·OEt$_2$ at −65 °C to solutions containing **10** leads to a neutral *trans* dicarbonyl [ν_{CO}(thf): 1976m and 1898s cm^{-1}] identified as the hydroxy carbene [WI{=C(OHMe)}(CO)$_2$(η-C$_5$H$_5$)] **12**. This reaction is not synthetically useful as many other uncharacterized products are also formed. A much better approach to **12** is the addition of SiMe$_3$Cl to **10** at low temperature followed by low-temperature filtration through a silica plug. Addition of SiMe$_3$Cl results in [WI{=C(OSiMe$_3$)Me}(CO)$_2$(η-C$_5$H$_5$)] **13**, which desilylates on silica to form **12** as a brown oil in an overall crude yield of 94%. As a consequence of this high lability, **13** is characterized by its IR spectrum only. The hydroxy carbene of **12** is indicated by the high-frequency ^{13}C NMR signal at δ_C 295.6. The OH group is indicated by a broad singlet in the ^{1}H NMR spectrum at δ_H 12.65 but the position and line shape of this signal are dependent on the degree of water contamination of the NMR solvent.

The hydroxy carbene **12** decomposes to uncharacterized complex mixtures in solvents other than thf or acetone. The reactive nature of hydroxy carbenes is recognized. The OH groups of hydroxy carbenes are known to behave as strong acids,[23] while there is also a tendency for hydroxycarbene ligands to be lost as aldehydes.[24]

Experimental

Infrared spectra were measured using a Perkin-Elmer 257 instrument, calibrated using the 1601.4 cm^{-1} absorption of polystyrene film, or on a Perkin-Elmer 1710 Fourier-transform instrument linked to a Perkin-Elmer 4600 Data Station. Variable-temperature IR spectra were obtained on the Perkin-Elmer 1710 instrument using a purpose built IR cell. Proton NMR spectra were recorded using a Bruker WP-80SY (80

MHz), Perkin-Elmer R34 (220 MHz), Bruker AM-250 (250 MHz) or Bruker WH-400 (400 MHz) spectrometer. Carbon-13 spectra were obtained using Bruker AM-250 (62.9 MHz) and Bruker WH-400 (100.6 MHz) instruments. Mass spectra were recorded using Kratos MS25 (electron impact mode), or Kratos MS80 [fast atom bombardment (FAB) mode] spectrometers.

All reactions were performed under nitrogen or argon atmospheres using deoxygenated solvents dried with an appropriate agent: thf from sodium-benzophenone, CH_2Cl_2 from CaH_2, and light petroleum (b.p. 40–60 °C throughout) from $LiAlH_4$. Diethyl ether was sodium dried. Brockman Activity II alumina and silica were used as supplied. The crown ether 12-crown-4 was dried as an approximately 1.0 mol dm^{-3} diethyl ether solution over CaH_2. The compound $[WMe(CO)_3(\eta\text{-}C_5H_5)]$ **5** was prepared by literature methods.[20] The boron compounds BEt_3 (Aldrich) and $LiBHEt_3$ (Aldrich 'Super Hydride') were used as solutions in thf as supplied and titrated periodically.

Preparation of Solutions containing $[WH(COMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ **6**.—A solution of $LiBHEt_3$ (2.0 cm^3, 2.0 mmol) was added to a solution of $[WMe(CO)_3(\eta\text{-}C_5H_5)]$ **5** (0.5 g, 1.43 mmol) in dry thf (50 cm^3) at room temperature. The solution darkened slightly from its initial bright yellow colour more or less instantly to form a solution containing the anion $[WH(COMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ **6** [ν_{CO}(thf); 1907m and 1816s cm^{-1}].

Preparation of $[Li(12\text{-crown-}4)_2][WH(COMe)(CO)_2(\eta\text{-}C_5H_5)]$.—Addition of 12-crown-4 as a solution in Et_2O (3.4 cm^3, 3.1 mmol) to a solution of **6** prepared as above resulted in no change in colour, or to the IR spectrum. Removal of solvent under vacuum gave an oily yellow solid. Washing with Et_2O (4 × 10 cm^3), and drying under vacuum, gave $[Li(12\text{-crown-}4)_2][WH(COMe)(CO)_2(\eta\text{-}C_5H_5)]$ as a pale yellow powder (0.79 g, 78%, m.p. 44–48 °C decomp.), which can be handled briefly in air. Similar yields are obtained by adding $LiBHEt_3$ to $[WMe(CO)_3(\eta\text{-}C_5H_5)]$ dissolved in Et_2O containing 12-crown-4, in which case the $[Li(12\text{-crown-}4)_2]^+$ salt of **6** precipitates directly from the reaction mixture [Found: M^- (negative ion FAB) 349. $C_9H_9O_3W$ requires M^- 349].

NMR Experiments monitoring the Reaction of $[WMe(CO)_3(\eta\text{-}C_5H_5)]$ **5** *with* $LiBHEt_3$.—In a typical experiment, freshly sublimed $[WMe(CO)_3(\eta\text{-}C_5H_5)]$ **5** (0.07 g, 0.20 mmol) was placed in an NMR tube and dissolved in thf (0.30 cm^3). After cooling to −70 °C, a solution of $LiBHEt_3$ (0.25 cm^3, 0.25 mmol) was layered slowly onto the thf solution of **5**, and the sample mixed with a thin glass rod after the $LiBHEt_3$ solution had cooled. Proton NMR spectra were recorded unlocked in the continuous-wave mode at 220 MHz, or at 250 MHz (Fourier transform) with solvent presaturation techniques. Carbon-13 NMR spectra at 100.6 MHz were obtained in mixed thf–[$^2H_8$]thf solvents. Additionally, the composition of all ^{13}C NMR samples was examined further by obtaining proton spectra immediately after acquisition of the ^{13}C NMR data.

Preparation of Solutions containing the Anion $[WI(COMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ **10**.—Addition of CHI_3 (0.45 g, 1.14 mmol) to a thf (40 cm^3) solution of $[Li(12\text{-crown-}4)_2][WH(COMe)(CO)_2(\eta\text{-}C_5H_5)]$ (0.80 g, 1.13 mmol) at −90 °C followed by warming to ambient temperature resulted in a brown solution whose IR spectrum contains four bands attributed to $[WI(COMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ [ν_{CO}(thf): 1937m, 1846s cm^{-1}] and the tricarbonyl **5** [ν_{CO}(thf): 2013s and 1917s cm^{-1}]. It is essential to use the solution promptly, since conversion of $[WI(COMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ to **5** is quite rapid at room temperature. These solutions are free of BEt_3.

Solutions containing BEt_3 were prepared as follows. A solution of $LiBHEt_3$ (1.2 cm^3, 1.2 mmol) was added to a solution of $[WMe(CO)_3(\eta\text{-}C_5H_5)]$ (0.3 g, 0.86 mmol) in dry thf (30 cm^3) at room temperature to form a solution containing the anion $[WH(COMe)(CO)_2(\eta\text{-}C_5H_5)]^-$. Iodoform (0.35 g, 0.88 mmol) was added after cooling the solution to −70 °C, after which the IR spectrum of the reaction mixture confirmed the formation of $[WI(COMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ [ν_{CO}(thf): 1937m and 1849s cm^{-1}] together with some **5** [ν_{CO}(thf): 2013s and 1917s cm^{-1}].

Progress of the reaction was monitored by NMR techniques by placing $[WMe(CO)_3(\eta\text{-}C_5H_5)]$ **5** (0.07 g, 0.20 mmol) in an NMR tube, dissolving it in thf (0.30 cm^3) and adding $LiBHEt_3$ (0.25 cm^3, 0.25 mmol). The tube was cooled to −90 °C and an excess of CHI_3 added. The ^1H NMR spectra were then recorded at 220 MHz as the solution approached ambient temperature.

Preparation of Solutions containing the Anion $[WCl(COMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ **9** *or* $[WBr(COMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ **8**.—The halides **8** and **9** are available in similar fashion by using appropriate quantities of CBr_4 or CCl_4. They are much more inclined to lose halide than does **10** and are therefore synthetically less useful. The NMR monitoring experiments were carried out in similar fashion to those of **10**.

Preparation of $[WI\{=C(OH)Me\}(CO)_2(\eta\text{-}C_5H_5)]$ **12**.—A solution containing $[Li(12\text{-crown-}4)_2][WH(COMe)(CO)_2(\eta\text{-}C_5H_5)]$ (0.46 g, 0.60 mmol) in dry thf (30 cm^3) was treated at −70 °C with CHI_3 (0.3 g, 0.8 mmol) to form $[WI(COMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ **10** as above. After addition of $SiMe_3Cl$ (0.1 cm^3, 0.8 mmol), the resulting solution was allowed to warm to 0 °C (1 h) after which the IR spectrum showed just two bands assigned to $[WI\{=C(OSiMe_3)Me\}(CO)_2(\eta\text{-}C_5H_5)]$ **13** [ν_{CO}(thf): 1927m and 1899s cm^{-1}]. The reaction mixture was filtered through silica (4 × 2 cm) at −50 °C to give an orange solution with an IR spectrum [ν_{CO}(thf): 1977m and 1899s cm^{-1}] of the product $[WI\{=C(OH)Me\}(CO)_2(\eta\text{-}C_5H_5)]$ **12**. The solvent was removed under vacuum to give crude **12** as an air-sensitive brown oil (0.30 g, 94%). The air sensitivity of the product precluded elemental analysis but the NMR spectra indicate the oil to be substantially pure. Attempted further purification led only to decomposition [Found: $(M - CH_4)^+$ 460. $C_9H_9IO_3W$ requires M 476]. The highest observed ion in the mass spectrum corresponds to $[WI(CO)_3(\eta\text{-}C_5H_5)]^+$, *i.e.* loss of methane. The IR spectrum of the bulk sample before and after the mass spectrum was recorded showed that the sample was still intact. The compound is too sensitive to record the IR spectrum as a KBr disc in order to identify the ν_{OH} stretch.

Similar yields are obtained from solutions of **6** generated from addition of $LiBHEt_3$ (0.8 cm^3, 0.8 mmol) to $[WMe(CO)_3(\eta\text{-}C_5H_5)]$ (0.2 g, 0.6 mmol) without work-up to remove BEt_3, and followed by the above method.

Preparation of $[WI\{=C(OMe)Me\}(CO)_2(\eta\text{-}C_5H_5)]$ **11**.—A solution containing $[Li(12\text{-crown-}4)_2][WH(COMe)(CO)_2(\eta\text{-}C_5H_5)]$ (0.8 g, 1.1 mmol) in dry thf (40 cm^3) was treated at −70 °C with CHI_3 (0.45 g, 1.2 mmol) to form $[WI(COMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ **10** as above. The solution was allowed to warm to −50 °C and $[Me_3O][BF_4]$ (0.5 g, 3.4 mmol) added. The reaction mixture was allowed to warm to room temperature slowly (1.5 h), during which time the colour changed from yellow to orange. Removal of the solvent, followed by chromatography on Al_2O_3 (12 × 2 cm) provided $[WMe(CO)_3(\eta\text{-}C_5H_5)]$ **5** (0.19 g, 50%) and a trace of $[WI(CO)_3(\eta\text{-}C_5H_5)]$ upon elution with light petroleum–CH_2Cl_2 (2:1). Elution with CH_2Cl_2 gave $[WI\{=C(OMe)Me\}(CO)_2(\eta\text{-}C_5H_5)]$ **11** as a dark oil which crystallized from CH_2Cl_2–hexane as orange microcrystals (0.12 g, 22%), m.p. 83–84 °C decomp. (Found: C, 24.5; H, 2.7%; M^+, 490. $C_{10}H_{11}IO_3W$ requires C, 24.5; H, 2.3%; M, 490).

Reaction of $[WI(CO)_3(\eta\text{-}C_5H_5)]$ *with* LiMe *and* $[Me_3O][BF_4]$.—A solution of LiMe in Et_2O (0.8 cm^3, 1.2 mmol) was added to a solution of $[\mathrm{WI(CO)_3(\eta\text{-}C_5H_5)}]$ (0.5 g, 1.08 mmol) in dry thf (50 $\mathrm{cm^3}$) at -80 °C and the solution allowed to warm to -50 °C. The IR spectrum at room temperature indicated only the formation of some **5** [ν_{CO}(thf): 2013s and 1917s $\mathrm{cm^{-1}}$] and $[\mathrm{W(CO)_3(\eta\text{-}C_5H_5)}]^-$ [ν_{CO}(thf): 1900s, 1801s, 1777s and 1715s $\mathrm{cm^{-1}}$]. An excess of $[\mathrm{Me_3O}][\mathrm{BF_4}]$ (0.4 g, 2.7 mmol) was added and the reaction allowed to come to room temperature slowly. Removal of the solvent followed by chromatography on $\mathrm{Al_2O_3}$ (10 × 1 cm) provided $[\mathrm{WMe(CO)_3(\eta\text{-}C_5H_5)}]$ (0.13 g, 35%) as the only significant product on elution with light petroleum–$\mathrm{CH_2Cl_2}$ (2:1).

Reaction of $[\mathrm{WH(COMe)(CO)_2(\eta\text{-}C_5H_5)}]^-$ **6** *with Water*.—A solution of $\mathrm{LiBHEt_3}$ (0.7 $\mathrm{cm^3}$, 0.5 mmol) was added to a solution of $[\mathrm{WMe(CO)_3(\eta\text{-}C_5H_5)}]$ (0.17 g, 0.5 mmol) in dry thf (10 $\mathrm{cm^3}$) at room temperature. A little water (0.05 $\mathrm{cm^3}$, 2.78 mmol) was added at room temperature. The reaction mixture darkened immediately and a gas (methane, GLC) was evolved. The IR spectrum [ν_{CO}(thf): 1900s, 1801s, 1777m and 1715s $\mathrm{cm^{-1}}$] indicated the formation of $\mathrm{Li}[\mathrm{W(CO)_3(\eta\text{-}C_5H_5)}]$. Iodine (0.13 g, 0.5 mmol) was added and the reaction stirred for 10 min. Removal of solvent followed by chromatography on $\mathrm{Al_2O_3}$ (10 × 1 cm) gave traces of **5** (0.002 g, 1%) and $[\mathrm{WI(CO)_3(\eta\text{-}C_5H_5)}]$ (0.039 g, 17%).

Acknowledgements

We should like to thank the SERC for funding and for the award of research studentships (to J. T. G. and S. W.).

References

1 J. A. Gladysz, *Adv. Organomet. Chem.*, 1982, **20**, 1.
2 P. Leoni, A. Landi and M. Pasquali, *J. Organomet. Chem.*, 1987, **321**, 365.
3 W. Tam, G.-U. Lin, W.-K. Wong, W. A. Kiel, V. K. Wong and J. A. Gladysz, *J. Am. Chem. Soc.*, 1982, **104**, 141.
4 W. Tam, M. Marsi and J. A. Gladysz, *Inorg. Chem.*, 1983, **22**, 1413.
5 J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, California, 2nd edn., 1987, and refs. therein.
6 J. A. Gladysz, G. M. Williams, W. Tam, D. L. Johnson, D. W. Parker and J. C. Selover, *Inorg. Chem.*, 1979, **18**, 553.
7 J. T. Gauntlett, B. F. Taylor and M. J. Winter, *J. Chem. Soc., Dalton Trans.*, 1985, 1815; *J. Chem. Soc., Chem. Commun.*, 1984, 420; J. T. Gauntlett and M. J. Winter, *Polyhedron*, 1986, **5**, 451.
8 J. T. Gauntlett, B. E. Mann, M. J. Winter and S. Woodward, *J. Organomet. Chem.*, 1988, **342**, C5.
9 F. A. Cotton and G. Wilkinson, in *Advanced Inorganic Chemistry*, Wiley-Interscience, New York, 5th edn., 1988, pp. 1034–1040 and refs. therein; A. R. Manning, *J. Chem. Soc. A*, 1967, 1984; P. Kubacek, R. Hoffmann and Z. Havlas, *Organometallics*, 1982, **1**, 180.
10 P. Leoni, E. Aquilini, M. Pasquali, F. Marchetti and M. Sabat, *J. Chem. Soc., Dalton Trans.*, 1988, 329; A. Asdar and C. Lapinte, *J. Organomet. Chem.*, 1987, **327**, C33.
11 J. R. Sweet and W. A. Graham, *J. Am. Chem. Soc.*, 1982, **104**, 2811.
12 D. Catheline, C. Lapinte and D. Astruc, *C.R. Acad. Sci. Paris, Ser. II*, 1985, **301**, 479; C. Lapinte, D. Catheline and D. Astruc, *Organometallics*, 1988, **7**, 1683.
13 A. Fratiello, R. Kubo and S. Chow, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1205.
14 D. J. Saturnino, M. Yamauchi, W. Y. Clayton, R. W. Nelson and S. G. Shore, *J. Am. Chem. Soc.*, 1975, **97**, 6063; R. K. Hertz, H. D. Johnson and S. G. Shore, *Inorg. Chem.*, 1973, **12**, 1875; C. A. Brown, *J. Organomet. Chem.*, 1978, **156**, C17 and refs. therein.
15 H. Hope, M. M. Olmstead, P. P. Power and X. Xu, *J. Am. Chem. Soc.*, 1984, **106**, 819; M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 1985, **107**, 2174; R. A. Bartlett and P. P. Power, *Organometallics*, 1986, **5**, 1916.
16 C. F. Lochow and R. G. Miller, *J. Am. Chem. Soc.*, 1976, **98**, 1281; J. W. Suggs, *J. Am. Chem. Soc.*, 1978, **100**, 640; R. E. Campbell, C. F. Lochow, K. P. Vora and R. G. Miller, *J. Am. Chem. Soc.*, 1980, **102**, 5824.
17 K. P. Darst and C. M. Lukehart, *J. Organomet. Chem.*, 1979, **171**, 65.
18 E. F. Landvatter and T. B. Rauchuff, *Organometallics*, 1982, **1**, 506; C. A. Ghilardi, S. Midollini, S. Moneti and A. Orlandini, *J. Chem. Soc., Dalton Trans.*, 1988, 1833; C. A. Tolman, S. D. Ittel, A. D. English and J. P. Jesson, *J. Am. Chem. Soc.*, 1979, **101**, 1742.
19 E. O. Fischer, U. Schubert, W. Kleine, H. Fischer, K. P. Darst, C. M. Lukehart, L. T. Warfield, D. J. Darensbourg, R. R. Burch and J. A. Frolich, *Inorg. Synth.*, 1978, **19**, 164, and refs. therein.
20 T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1956, **3**, 104.
21 N. A. Bailey, P. L. Chell, C. P. Manuel, A. Mukhopadhyay, D. Rogers, H. E. Tabbron and M. J. Winter, *J. Chem. Soc., Dalton Trans.*, 1983, 2397.
22 T. Kruck, M. Hofler and L. Liebig, *Chem. Ber.*, 1972, **105**, 1174; T. Kruck and L. Liebig, *Chem. Ber.*, 1973, **106**, 3661.
23 K. R. Grundy and W. R. Roper, *J. Organomet. Chem.*, 1981, **216**, 255.
24 K. P. Darst, P. G. Lenhert, C. M. Lukehart and L. T. Warfield, *J. Organomet. Chem.*, 1980, **195**, 317.

Received 28*th November* 1990; *Paper* 0/05372D