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FLUXIONALITY OF M_2C_2 TETRAHEDRAL CLUSTERS CONTAINING CYCLOPENTADIENYLDICARBONYLMETAL VERTICES: UNEXPECTEDLY DIFFERENT BEHAVIOUR OF MOLYBDENUM AND TUNGSTEN ANALOGUES

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Summary

The syntheses of a series of molecules $[Cp'M(CO)_2]_2(RC{\equiv}CR')$, where Cp' = C_5Me_5, C_5H_4Me; M = Mo, W; R = Ph, R' = H, Et, CO_2Me, $SnMe_3$ are described. The molybdenum complexes possess a semi-bridged carbonyl thus rendering the molecules chiral; their ^{13}C NMR spectra show four carbonyl resonances and two cyclopentadienyl environments. The barrier to racemisation depends on the bulk of the substituents on the ring. In contrast, the NMR spectra of the tungsten analogues show only single carbonyl and cyclopentadienyl environments even at −90°C and 9.4 T.

Introduction

In continuation of our studies on fluxionality in organotransition metal clusters [1,2], we chose to attempt the synthesis of an $M_2M'C_2$ trimetal-alkyne cluster in which all five vertex atoms are NMR active. Furthermore, we needed these vertex atoms with spin quantum number $I = \frac{1}{2}$ so that any temperature dependence of the metal–metal or metal–carbon coupling constants could be readily monitored; with these data it was hoped that changes in molecular geometry could be inferred. Earlier work [3–6] had indicated that a viable route might involve the capping of a tetrahedral precursor of the type M_2C_2 and, since M' can be varied, some control over the structure of the final cluster can be gained. We now present data on the dynamic properties of several M_2C_2 clusters which may be viable precursors for the expansion reactions outlined above.

Results and discussion

Several years ago, Cotton [7] reported that molecules of the type $Cp_2Mo_2(CO)_4(RC{\equiv}CR')$ did not adopt the expected C_{2v} geometry (or C_s, if $R \neq R'$) but

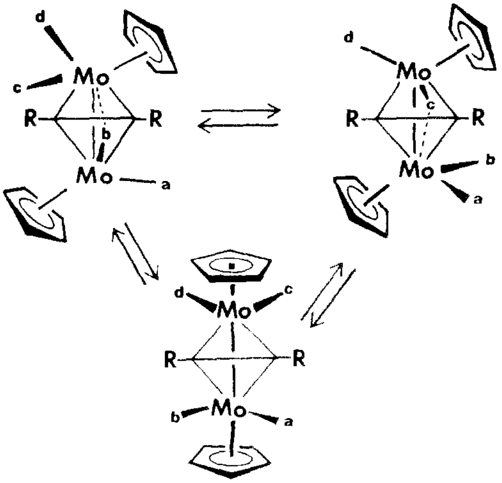

Fig. 1. Semi-bridging carbonyl exchange process.

instead possessed C_1 symmetry and were thus chiral. This situation arose because the four carbonyls did not bond equivalently, indeed, one was clearly semi-bridging and so rendered the other three non-equivalent. The dynamic ^{13}C NMR spectra were entirely consistent with the crystallographic data: at low temperature, the molecules exhibited four different carbonyl resonances and two cyclopentadienyl environments. Upon warming the solution, exchange between the semi-bridging carbonyl and a terminal carbonyl on the other molybdenum was observed. Subsequently, partial rotation about the Mo–Mo vector occurs with a somewhat higher activation energy barrier. As shown in Fig. 1, this has the effect of equilibrating the cyclopentadienyl groups and generating only two carbonyl environments; for the molecules in which R = R′ the system possesses time-averaged C_{2v} symmetry and only a single carbonyl resonance is seen. No evidence of exchange of carbonyl groups between metals was observed although such exchange has been detected in $Cp_2MoW(CO)_4$ [8]. In the particular case where R = R′ = Et, a plethora of carbonyl resonances was observed at low temperature and Cotton chose not to speculate at length about the details of the spectra. In retrospect, we offer the comment that, in view of the known multiplicity of rotamers available to poly-ethylated ligands [9,10], the data are probably rationalisable in terms of several co-existing conformers differing only in the relative orientations of the ethyl groups.

In the course of our synthetic studies aimed at generating M_2C_2 clusters as precursors to $M_2M'C_2$ systems, we prepared a series of molecules of the type $Cp^{\star}_2M_2(CO)_4(RC{\equiv}CR')$, where $Cp^{\star} = C_5Me_5$ or C_5H_4Me, M = Mo or W, R = Ph, and R′ = H or CO_2Me. With these in hand, we decided to extend Cotton's work to include molecules containing bulky cyclopentadienyl units to compare the activation energy parameters with those previously reported. The carbonyl infrared data clearly indicate the presence of semi-bridging carbonyls in these molecules, likewise the low temperature ^{13}C NMR spectra of the molybdenum complexes exhibited four carbonyl resonances which coalesced at high temperature entirely in keeping with Cotton's proposal. The activation energy parameters for these molecules were obtained from

TABLE 1

$\Delta G^{\#}$ FOR THE COMPLEXES $[CpM(CO)_2]_2RC{\equiv}CR'$ (M = Mo, W)

Cyclopentadienyl ligand	Metal	Acetylene	$\Delta G^{\#}$ (kcal mol^{-1})
C_5H_5 [a]	Mo	$PhC{\equiv}CH$	9.6 ± 0.2
$CH_3C_5H_4$	Mo	$PhC{\equiv}CH$	10.0 ± 0.2
$CH_3C_5H_4$	Mo	$PhC{\equiv}CCO_2CH_3$	10.5 ± 0.3
$(CH_3)_5C_5$	Mo	$PhC{\equiv}CH$	12.6 ± 0.3
$(CH_3)_5C_5$	W	$PhC{\equiv}CH$	–
$CH_3C_5H_4$	W	$PhC{\equiv}CCO_2CH_3$	–

[a] See ref. 7.

the ^1H and ^{13}C NMR spectra of the cyclopentadienyl methyl resonances and also by simulation of the ^{13}C spectra in the carbonyl region. Typically, the "low energy" bridging-terminal carbonyl process has a barrier of ca. 8 kcal mol^{-1}. The $\Delta G^{\#}$ values for the "higher energy process" are collected in Table 1. The larger barriers are, presumably, a reflection of the increased steric problems caused by the bulk of the methyl groups introduced into the cyclopentadienyl ring and the consequently increased tendency of the molecule to adopt the semi-bridged carbonyl structure to alleviate the molecular crowding.

Whilst the bulky molybdenum complexes followed the reactivity pattern anticipated from that previously reported, we were somewhat surprised at the behaviour of the analogous tungsten systems. One would have perhaps predicted that the fluxional behaviour of $[(C_5Me_5)W(CO)_2]_2(PhC{\equiv}CH)$ would mirror that of the molybdenum analogue and that, since structural differences between Mo and W analogues are minimal [7,11], the activation energies would also be similar. However, the ^{13}C and ^1H NMR spectra of $[(C_5Me_5)W(CO)_2]_2(PhC{\equiv}CH)$, recorded at −100°C at a field of 9.4 T (100.6 MHz for ^{13}C; 400 MHz for protons) exhibit only a single carbonyl resonance and a single pentamethylcyclopentadienyl environment. By way of contrast, the corresponding molybdenum complex (see Fig. 2) showed four carbonyl resonances and two different pentamethylcyclopentadienyl environments at −40°C on the same spectrometer. Since the infrared spectrum of the W complex clearly indicates the presence of a semi-bridging carbonyl, it is apparent that the barrier to exchange must be considerably less than that measured for the molybdenum case, assuming that chemical shift differences are comparable. The same behaviour is observed with the monomethylcyclopentadienyl derivatives of Mo and W.

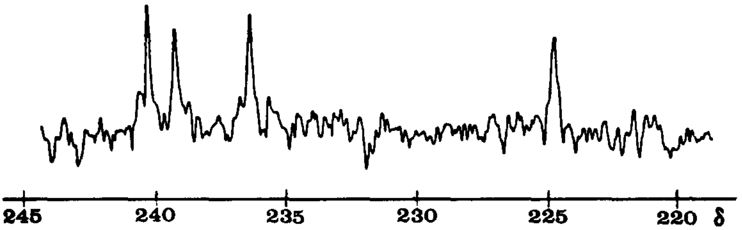

Fig. 2. Section of the 100.613 MHz ^{13}C NMR spectrum of $[(C_5Me_5)Mo(CO)_2]_2(PhC{\equiv}CH)$ in the metal carbonyl region.

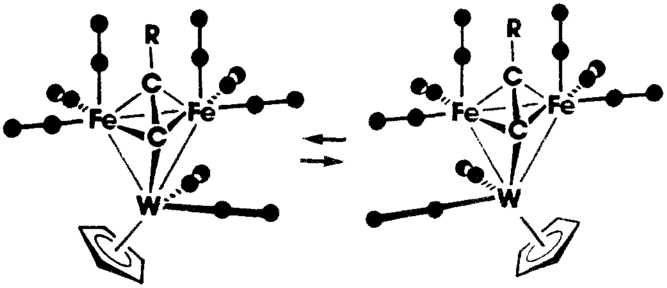

Fig. 3. Rotation of a CpW(CO)$_2$ fragment relative to an Fe$_2$C triangular face.

In seeking a literature precedent for such strikingly different behaviour between closely analogous molybdenum and tungsten complexes, we noted the fluxionality of the bridged acetylide complexes CpM(CO)$_2$Fe$_2$(CO)$_6$(μ-C$_2$R), where M = Mo or W [12]. These molecules adopt a pseudo-trigonal bipyramidal geometry in which the two Fe(CO)$_3$ moieties and the carbido carbon comprise the equatorial plane and the alkylidyne and CpM(CO)$_2$ fragments are the capping units. The carbonyls bonded to the axial tungsten (or molybdenum) atom are twisted such that there is no plane of symmetry and so these carbonyls are magnetically non-equivalent. This asymmetry is reflected in the ^{13}C NMR spectrum of the molybdenum complex which exhibits two carbonyl resonances; in contrast, the two tungsten-bonded carbonyls (which are unequivocally identified by their ^{183}W satellites) are equilibrated by a dynamic process even at −90°C. In this latter case, as with the molecules described earlier, one can propose that the CpW(CO)$_2$ moiety rotates around an axis through the tungsten atom and a C$_2$W (or Fe$_2$C) triangular face with a much lower barrier than for their molybdenum congeners. We note that the complexes $[(C_5H_5)W(CO)_2]_2(RC{\equiv}CR)$, where R = H, CO$_2CH_3$, CF$_3$ or C$_6$H$_4$CH$_3$, have been synthesised [13–17], but we are unaware of any low temperature NMR data on these molecules. Interestingly, however, recent work from Shriver's laboratory [18] indicates that in the tetrahedral $[Fe_3M(CO)_{14}]^{2-}$ systems, where M = Cr, Mo, W, the fluxionality of the carbonyls can be stopped on the NMR time scale for the Cr and Mo complexes but not for the W analogue.

Any proposed rationale to account for the differences between CpMo(CO)$_2$ and CpW(CO)$_2$ must go beyond the usual form of the isolobal analogy which would relate these two organometallic units to the CH fragment. Hoffmann [19] has pointed out that the remnants of the t_{2g} set, although less directional than the frontier orbitals, may still become involved in the bonding. This aspect has been amplified by Evans [20] who rationalised the reluctance of the third row metals to form bridging carbonyls in terms of the stabilisation of the t_{2g} orbitals by π-bonding with the terminal carbonyl ligands. Perhaps enhanced participation by the remnants of the t_{2g} set in W=C=O and W–Cp π-bonding results in a less localised interaction of the fragment to a triangular face than is the case for the molybdenum complexes. Hence, free rotation of the capping moiety has a lower barrier for the third row metal in these cases. It will be interesting to see whether other examples of such behaviour emerge in the near future.

A further point of interest is the ease with which acetylenes add to molybdenum–molybdenum triple bonds under thermal conditions whereas, in the case of tungsten, only alkynes bearing electron-withdrawing groups give products – and even then the yields are not always very good! However, under photochemical conditions, previously unreactive acetylenes give the desired products [13,16]. The primary photoprocess upon UV irradiation of $[CpW(CO)_3]_2$ has been shown to be homolytic fission of the tungsten–tungsten bond [16,21]; indeed, this also appears to be the case with the pentamethylcyclopentadienyl tungsten dimer which gives mainly $Cp^*W(CO)_3SnMe_3$ in the photochemical reaction of $Cp^*_2W_2(CO)_6$ with $PhC{\equiv}CSnMe_3$. Presumably, this reaction proceeds via an S_H2 radical substitution mechanism [22].

To conclude, we report the syntheses of a variety of di-molybdenum and di-tungsten alkyne complexes in which the metals bear bulky cyclopentadienyl groups. The former show restricted rotation about the metal–metal bond while the latter do not. Furthermore, while there is no evidence of intermetallic carbonyl scrambling in the Mo–Mo complexes, this process does appear to be occurring for the W–W analogues. This behaviour parallels the carbonyl scrambling already known [8] for $Cp_2MoW(CO)_4$ *.

Experimental

All preparations were carried out under an atmosphere of dry nitrogen. Solvents were dried according to standard procedures [23]. Mass spectra were obtained using a VG-7070F mass spectrometer equipped with a VG 2035 data system. All compounds exhibited correct isotope distribution patterns. Masses quoted are for the most abundant metal isotope. Infrared spectra were recorded on a Perkin–Elmer 283 instrument using either KBr solution cells or NaCl plates. NMR spectra were recorded using Bruker WM 400, WM 250 or WP 80 spectrometers. ^1H and ^{13}C chemical shifts are reported relative to tetramethylsilane; ^{119}Sn shifts were measured relative to tetramethylstannane. Unless otherwise stated, all NMR data reported were recorded at ambient temperature.

$[(MeCp)M(CO)_3]_2$ (M = Mo, W) was prepared according to the method of Manning et al. [24].
Mo: ^1H NMR (C_6D_6) δ, 4.85 (Cp-H's), 1.8 (Me); ^{13}C NMR (C_6D_6) δ, 108.2 (Cp*C*), 93.05, 91.95 (Cp*CH*), 13.86 (Me); ^{95}Mo NMR (C_6D_6) δ (relative to MoO_4^{2-}), -2784, $W_{\frac{1}{2}}$ 250 Hz. IR (C_6H_{12}) 1990w, 1960s, 1915s, 1910m cm^{-1}. Mass spectrum, *m/z* (%), 466(20) $C_{16}H_{14}O_4Mo_2$, 438(6) $C_{15}H_{14}O_3Mo_2$, 410(10) $C_{14}H_{14}O_2Mo_2$, 354(10) $C_{12}H_{14}Mo_2$, 261(15) $C_9H_7O_3Mo$, 233(20) $C_8H_7O_2Mo$, 205(11) C_7H_7OMo, 177(100) C_6H_7Mo.
W: ^1H NMR (C_6D_6) δ, 4.90 (Cp-H's), 1.9 (Me); ^{13}C NMR (C_6D_6) δ, 106.56 (Cp*C*), 92.28, 90.17 (Cp*CH*), 13.85 (Me). IR (C_6H_{12}) 1980s, 1950s, 1910s, 1895m, 1850vw cm^{-1}. Mass spectrum, *m/z* (%), 694(1) $C_{18}H_{14}O_6W_2$, 666(5) $C_{17}H_{14}O_5W_2$, 638(8) $C_{16}H_{14}O_4W_2$, 610(1) $C_{15}H_{14}O_3W_2$, 582(7) $C_{14}H_{14}O_2W_2$, 554(1) $C_{13}H_{14}OW_2$, 526(8) $C_{12}H_{14}W_2$, 347(30) $C_9H_7O_3W$, 319(25) $C_8H_7O_2W$, 291(20), C_7H_7OW, 263(100) C_6H_7W.

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* *Note added in proof.* A very recent report has appeared concerning molecules of the type $Cp'Cp''W_2(CO)_4R_2C_2$ possessing very bulky substituents in the Cp rings. In these cases, carbonyl fluxionality can be stopped on the NMR time-scale at low temperature [27].

$[(C_5Me_5)M(CO)_3]_2$ (M = Mo, W) was prepared according to the method of King et al. [25].

Mo: ^{1}H NMR (CD_2Cl_2) δ, 1.94 (Me); ^{13}C NMR, CD_2Cl_2, δ, 96.12 (*C*Me), 9.6 (Me). IR (C_6H_6) 1933m, 1898m cm^{-1}. Mass spectrum, *m/z* (%), 578(18) $C_{24}H_{30}O_4Mo_2$, 550(10) $C_{23}H_{30}O_3Mo_2$, 522(10) $C_{22}H_{30}O_2Mo_2$, 494(2) $C_{21}H_{30}OMo_2$, 466(20) $C_{20}H_{30}Mo_2$, 317(10) $C_{13}H_{15}O_3Mo$, 289(5) $C_{12}H_{15}O_2Mo$, 261(10) $C_{11}H_{15}OMo$, 233(75) $C_{10}H_{15}Mo$, 135(12) $C_{10}H_{15}$, 105(100) C_7H_5O.

W: ^{1}H NMR ($CDCl_3$) δ, 2.05 (Me). IR (C_6H_6) 1920m, 1893m cm^{-1}. Mass spectrum, *m/z* (%), 806(1) $C_{26}H_{30}O_6W_2$, 750(1) $C_{24}H_{30}O_4W_2$, 694(1) $C_{22}H_{30}O_2W_2$, 403(10) $C_{13}H_{15}O_3W$, 375(1) $C_{12}H_{15}O_2W$, 347(5) $C_{11}H_{15}OW$, 135(50) $C_{10}H_{15}$, 105(100) C_7H_5O.

Metal–metal triple bonded complexes were prepared from the corresponding single bonded precursors following the method of Wrighton et al. [11].

Phenylacetylene, diphenylacetylene and acetylenedicarboxylic acid dimethyl ester were purchased from Aldrich and used without further purification. 1-Phenylbutyne was purchased from Columbia Chemicals and used without further purification. Methyl phenylpropiolate was prepared by the method described in Vogel [26]. b.p. 80–82°C/0.2 mmHg; ^{1}H NMR ($CDCl_3$) δ, 7.6, 7.55, 7.4 (Ph), 3.8 (OMe); ^{13}C NMR ($CDCl_3$) δ, 154.27 (C=O), 132.83, 130.52, 128.44, 120.46 (Ph), 86.33, 80.31 (C≡C), 52.58 (OMe); IR, (neat), 2235 (C≡C), 1720 (C=O) cm^{-1}; mass spectrum, *m/z* (%), 160(20) $C_{10}H_8O_2$, 129(100) C_9H_5O, 102(30) C_8H_6. 2-Phenylethynyltrimethyltin was prepared via the reaction of chlorotrimethyltin with lithium phenylacetylide in diethyl ether; ^{1}H NMR ($CDCl_3$) δ, 7.13 (Ph), 0.3 (Sn-Me) [$^2J(^{119}Sn{-}H)$ 64 Hz]; ^{13}C NMR ($CDCl_3$) δ, 131.9, 128.1, 123.6 (Ph), 109.0, 93.2 (C≡C), −7.7 (Sn-Me) [$^1J(^{119}Sn{-}C)$ 397.1 Hz]; ^{119}Sn NMR, $CDCl_3$, δ, −68.66; IR, neat, (C≡C) 2125 cm^{-1}; mass spectrum, *m/z* (%), 264(5) $C_{11}H_{14}Sn$, 249(100) $C_{10}H_{11}Sn$, 219(75), C_8H_5Sn, 163(60) C_3H_9Sn, 133(10) CH_3Sn, 118(10) Sn.

$[(C_5Me_5)Mo(CO)_2)]_2PhC{\equiv}CH$

$[(C_5Me_5)Mo(CO)_2)]_2$ (0.3 g, 0.52 mmol) and phenylacetylene (0.056 g, 0.55 mmol) were heated under reflux in hexane during 24 h. After cooling and filtration, the reaction mixture was chromatographed on silica gel. Elution with hexane gave orange $[(C_5Me_5)Mo(CO)_2)]_2$; upon increasing the polarity to chloroform/hexane (1/4), the desired product was obtained as a red band (0.134 g, 0.20 mmol; 38%); ^{1}H NMR ($CDCl_3$) δ, 7.3 (Ph), 5.10 (CH), 1.85 (Me); ^{13}C NMR (CD_2Cl_2) (9.4 T) 193 K, δ, 240.83, 239.80, 236.96, 225.34 (C≡O), 131.00, 129.53, 128.63, 127.62 (Ph), 102.81, 101.75 (*C*Me), 10.47, 9.60 (Me). IR (C_6H_{12}) 1990m, 1980m, 1920s, 1905m, 1825w cm^{-1}. Mass spectrum, *m/z* (%), 624(1.5) $C_{30}H_{36}O_2Mo_2$, 596(0.5) $C_{29}H_{36}OMo_2$, 579(1) $C_{24}H_{31}O_4Mo_2$, 568(0.5) $C_{28}H_{36}Mo_2$, 551(0.8) $C_{23}H_{31}O_3Mo_2$, 523(1) $C_{22}H_{31}O_2Mo_2$, 495(1.5) $C_{21}H_{31}OMo_2$, 467(0.8) $C_{20}H_{31}Mo_2$, 317(2) $C_{13}H_{15}O_3Mo$, 289(15) $C_{12}H_{15}O_2Mo$, 261(2) $C_{11}H_{15}OMo$, 233(0.5) $C_{10}H_{15}Mo$, 135(30) $C_{10}H_{15}$, 105(100) C_7H_5O.

$[(C_5Me_5)Mo(CO)_2)]_2MeO_2CC{\equiv}CCO_2Me$

In an analogous fashion, $[(C_5Me_5)Mo(CO)_2)]_2$ and $MeO_2CC{\equiv}CCO_2Me$ gave a 37% yield of red crystals (from hexane). ^{1}H NMR ($CDCl_3$) δ, 3.82 (OMe), 2.0 (Me); ^{13}C NMR ($CDCl_3$) δ, 237.79, 236.84 (C≡O), 152.83 (C=O), 53.82 (OMe), 10.54 (Me). IR (C_6H_{12}) 1990w, 1970s, 1930m, 1856m, 1720 (asym. ester), 1685 (sym. ester) cm^{-1}.

$[(C_5Me_5)Mo(CO)_2)]_2PhC{\equiv}CEt$

Analogously, the desired product was obtained but only in trace quantities. ^1H NMR ($CDCl_3$) δ, 7.3 (Ph), 2.4 (CH_2), 1.98 (C_5Me_5), 1.2 (CH_3). IR (C_6H_{12}) 1990w, 1980m, 1975m, 1930m, 1905m, 1820w cm^{-1}.

$[(C_5Me_5)Mo(CO)_2)]_2PhC{\equiv}CSnMe_3$

$[(C_5Me_5)Mo(CO)_2)]_2$ (0.3 g, 0.52 mmol) and $PhC{\equiv}CSnMe_3$ (0.14 g, 0.53 mmol) were stirred for 36 h in hexane. Chromatography on silica gel, as above, yielded the product (0.21 g, 0.25 mol; 48%). ^1H NMR ($CDCl_3$) δ, 7.35 (Ph), 1.95 (C_5Me_5), 0.35 ($SnMe_3$) [$^2J(^{119}Sn-H)$ 60 Hz]. IR (C_6H_{12}) 1970w, 1945s, 1910m, 1890w cm^{-1}. Mass spectrum, *m/z* (%), 730(0.5) $C_{31}H_{44}Mo_2Sn$, 679(0.4) $C_{32}H_{35}O_4Mo_2$, 578(1) $C_{24}H_{30}O_4Mo_2$, 567(1) $C_{28}H_{35}Mo_2$, 551(2) $C_{23}H_{31}O_3Mo_2$, 523(2) $C_{22}H_{31}O_2Mo_2$, 495(0.5) $C_{21}H_{31}OMo_2$, 467(10) $C_{20}H_{31}Mo_2$, 465(1) $C_{15}H_{21}O_3MoSn$, 437(1) $C_{14}H_{21}O_2MoSn$, 409(1) $C_{13}H_{21}OMoSn$, 381(1) $C_{12}H_{21}MoSn$, 366(1) $C_{11}H_{18}MoSn$, 351(1) $C_{10}H_{15}MoSn$, 317(8) $C_{13}H_{15}O_3Mo$, 289(4) $C_{12}H_{15}O_2Mo$, 261(4) $C_{11}H_{15}OMo$, 233(20) $C_{10}H_{15}Mo$, 219(50) C_8H_5Sn, 163(50) C_3H_9Sn, 148(18) C_2H_6Sn, 135(40) $C_{10}H_{15}$, 133(25) CH_3Sn, 118(15) Sn, 105(100) C_7H_5O.

$[(CH_3C_5H_4)Mo(CO)_2]_2PhC{\equiv}CH$

$[(CH_3C_5H_4)Mo(CO)_3]_2$ (1.0 g, 1.9 mmol) and phenylacetylene (0.2 g, 2 mmol) were heated under reflux for 16 h in petroleum ether (100–120°C). After cooling, filtration and removal of solvent, the residue was chromatographed on silica gel and elution with hexane produced the desired complex (0.25 g, 0.44 mmol; 23%). ^1H NMR (C_6D_6) δ, 7.25 (Ph), 5.42 (CH), 5.1 (Cp-H's), 2.05 (Me); ^{13}C NMR (CD_2Cl_2) (5.9 T) δ, 232.67, 230.91, 227.98, 227.47 (C≡O), 130.11, 129.14, 128.15, 125.42 (Ph), 109.1 (Cp*C*), 93.56, 92.12 (Cp*C*H), 78.82, 65.75 (C≡C), 14.46 (Me). IR (C_6H_{12}) 1980m, 1915s, 1836w cm^{-1}. Mass spectrum, *m/z* (%), 568(1.5) $C_{24}H_{20}O_4Mo_2$, 512(2) $C_{22}H_{20}O_2Mo_2$, 484(1) $C_{21}H_{20}OMo_2$, 466(3), $C_{16}H_{14}O_4Mo_2$, 456(8) $C_{20}H_{20}Mo_2$, 438(3) $C_{15}H_{14}O_3Mo_2$, 410(3) $C_{14}H_{14}O_2Mo_2$, 382(0.5) $C_{13}H_{14}OMo_2$, 354(1) $C_{12}H_{14}Mo_2$, 261(15) $C_9H_7O_3Mo$, 233(20) $C_8H_7O_2Mo$, 205(11) C_7H_7OMo, 177(10) C_6H_7Mo, 98(30) Mo, 77(100) C_6H_5.

$[(CH_3C_5H_4)Mo(CO)_2]_2PhC{\equiv}CCO_2Me$

$[(CH_3C_5H_4)Mo(CO)_3]_2$ (0.5 g, 0.95 mmol) and $PhC{\equiv}CCO_2Me$ (0.16 g, 1 mmol) were heated under reflux in petroleum ether (100–120°C) for 18 h. Chromatography on Brockman Grade 1 neutral alumina using hexane/diethyl ether (6/1) gave $[(CH_3C_5H_4)Mo(CO)_2]_2$; elution with diethyl ether alone yielded the desired product (0.078 g, 0.12 mmol; 13%); ^1H NMR (CD_2Cl_2) δ, 7.25 (Ph), 5.08 (Cp-H's), 3.73 (OMe), 2.02 (Me); ^{13}C NMR (CD_2Cl_2) (5.9 T) δ, 231.25, 225.56, 220.38, 215.2 (C≡O), 176.9 (C=O), 128.21, 127.52, 125.32 (Ph), 107.2 (Cp*C*Me), 94.18, 90.43 (Cp*C*H), 82.6, 71.1 (C≡C), 52.62 (OMe), 12.99 (Me). IR (C_6H_6) 1990m, 1935s, 1830w, 1735, 1681 (ester) cm^{-1}. Mass spectrum, *m/z* (%), 626(2) $C_{26}H_{22}O_6Mo_2$, 570(2) $C_{24}H_{22}O_4Mo_2$, 567(4) $C_{24}H_{19}O_4Mo_2$, 542(2) $C_{23}H_{22}O_3Mo_2$, 511(6) $C_{22}H_{19}O_2Mo_2$, 490(5) $C_{18}H_{14}O_4Mo_2$, 410(1) $C_{14}H_{14}O_2Mo_2$, 261(10) $C_9H_7O_3Mo$, 233(15) $C_8H_7O_2Mo$, 177(20) C_6H_7Mo, 160(10) $C_{10}H_8O_2$, 129(20) C_9H_5O, 105(100) C_7H_5.

$[(C_5Me_5)W(CO)_2]_2PhC{\equiv}CH$

$[(C_5Me_5)W(CO)_3]_2$ (0.5 g, 0.62 mmol) and phenylacetylene (0.074 g, 0.73 mmol) in toluene (30 cm^3) were irradiated at 254 nm for 48 h using a Rayonet Photoreactor. After filtration and removal of toluene in vacuo, the resulting mixture was recrystallised from benzene/pentane to give the desired product (25.6 mg, 0.03 mmol; 5%): ^{1}H NMR (C_6D_6) δ, 7.4 (Ph), 5.35 (CH), 2.22 (Me); ^{13}C NMR (CD_2Cl_2) (9.4 T) 193 K, δ, 191.61 (C≡O), 131.96, 129.06, 128.45, 127.85 (Ph), 120.1 (CpC), 10.4 (Me). IR (C_6H_6) 1983m, 1920m, 1905sh, 1860w cm^{-1}. Mass spectrum, *m/z* (%), 796(0.5) $C_{30}H_{36}O_2W_2$, 740(0.5) $C_{28}H_{36}W_2$, 723(1.5) $C_{23}H_{31}O_3W_2$, 695(0.5) $C_{22}H_{31}O_2W_2$, 667(0.3) $C_{21}H_{31}OW_2$, 639(0.5) $C_{20}H_{31}W_2$, 403(3) $C_{13}H_{15}O_3W$, 375(1.5) $C_{12}H_{15}O_2W$, 347(2) $C_{11}H_{15}OW$, 319(5) $C_{10}H_{15}W$, 135(25) $C_{10}H_{15}$, 105(100) C_7H_5O.

$[(C_5Me_5)W(CO)_2]_2PhC\equiv CSnMe_3$

$[(C_5Me_5)W(CO)_3]_2$ (0.5 g, 0.62 mmol) and PhC≡CSnMe$_3$ (0.17 g, 0.64 mmol) were photolysed for 15 h, as described above. However, in this reaction, a white solid deposited in the bottom of the quartz reaction vessel and this was identified as $(C_5Me_5)W(CO)_3SnMe_3$ (0.18 g, 0.32 mmol; 50%). ^{1}H NMR ($CDCl_3$) δ, 2.1 (CpMe), 0.55 (SnMe) [$^2J(^{119}Sn-H)$ 64 Hz]. IR (C_6H_6) 1970m, 1930m, 1890w cm^{-1}. Mass spectrum, *m/z* (%), 551(1) $C_{15}H_{21}O_3SnW$, 510(1) $C_{14}H_{24}OSnW$, 482(1) $C_{13}H_{20}SnW$, 403(2) $C_{13}H_{15}O_3W$, 375(2) $C_{12}H_{15}O_2W$, 347(2) $C_{11}H_{15}OW$, 319(3) $C_{10}H_{15}W$, 165(100) C_3H_9Sn, 149(15) C_2H_6Sn, 135(4) $C_{10}H_{15}$, 133(20) CH_3Sn. The remaining toluene solution was evaporated to dryness and the residue recrystallised from chloroform/pentane to give a low yield of the desired product (50 mg, 0.05 mmol; 8%): ^{1}H NMR ($CDCl_3$) δ, 7.3 (Ph), 2.0 (CpMe), 0.5 (SnMe) [$^2J(^{119}Sn-H)$ 69 Hz]; ^{13}C NMR ($CDCl_3$) δ, 131.0, 130.0, 128.5, 121.5 (Ph), 118.5 (CpC), 11.27 (Cp*Me*), 1.2 (Sn*Me*) [$^1J(^{119}Sn-C)$ 397 Hz]; ^{119}Sn NMR ($CDCl_3$) δ, 14.2. IR (C_6H_6) 1990w, 1975w, 1943s, 1885w cm^{-1}.

$[(CH_3C_5H_4)W(CO)_2]_2PhC\equiv CCO_2Me$

$[(CH_3C_5H_4)W(CO)_2]_2$ (0.5 g, 0.78 mmol) and PhC≡CCO$_2$Me (0.13 g, 0.81 mmol) were heated under reflux in 100 cm^3 petroleum ether (100–120°C) for 18 h. Chromatography on Brockman Grade 1 neutral alumina using hexane as eluent gave $[(CH_3C_5H_4)W(CO)_2]_2$ and, upon increasing the polarity by using methylene chloride, the desired product (36.5 mg, 0.045 mmol; 6%): ^{1}H NMR (CD_2Cl_2) δ, 7.25 (Ph), 5.13, 5.10 (CpH), [J(HH) 2.5 Hz], 3.72 (OMe), 2.17 (CpMe); ^{13}C NMR (CD_2Cl_2) (5.9 T) δ, 190.2 (C≡O), 175.4 (C=O), 129.5, 128.9, 128.2, 120.0 (Ph), 107.3, (CpCMe), 93.0, 92.2 (CpCH), 52.5 (OMe), 13.18 (Me). IR (C_6H_6) 1990m, 1920s, 1825w, 1735, 1681 (ester) cm^{-1}. Mass spectrum, *m/z* (%), 742(4) $C_{24}H_{22}O_4W_2$, 739(2) $C_{24}H_{19}O_4W_2$, 718(1) $C_{23}H_{22}O_3W_2$, 714(3) $C_{23}H_{22}O_3W_2$, 686(1) $C_{22}H_{22}O_2W_2$, 658(15) $C_{21}H_{22}OW_2$, 634(4) $C_{17}H_{14}O_3W_2$, 606(2) $C_{16}H_{14}O_2W_2$, 578(2) $C_{15}H_{14}OW_2$, 550(2) $C_{14}H_{14}W_2$, 347(3) $C_9H_7O_3W$, 319(3) $C_8H_7O_2W$, 291(5) C_7H_7OW, 263(2) C_6H_7W, 160(30) $C_{10}H_8O_2$, 129(100) C_9H_5O.

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References

1 M.J. McGlinchey, M. Mlekuz, P. Bougeard, B.G. Sayer, A. Marinetti, J.-Y. Saillard and G. Jaouen, Can. J. Chem., 61 (1983) 1319.

2 M. Mlekuz, P. Bougeard, B.G. Sayer, S. Peng, M.J. McGlinchey, A. Marinetti, J.-Y. Saillard, J. Ben Naceur, B. Mentzen and G. Jaouen, Organometallics, 4 (1985) 1123.
3 G. Jaouen, A. Marinetti, B. Mentzen, R. Mutin, J.-Y. Saillard, B.G. Sayer, and M.J. McGlinchey, Organometallics, 1 (1982) 753.
4 F.W.B. Einstein, B.H. Freeland, K.G. Tyers, D. Sutton and J.M. Waterous, J. Chem. Soc., Chem. Commun., (1982) 371.
5 M.I. Bruce, J.R. Rodgers, M.R. Snow and F.S. Wong, J. Organomet. Chem., 240 (1982) 299.
6 J.F. Tilney-Bassett, J. Chem. Soc., (1963) 4784.
7 W.I. Bailey, Jr., M.H. Chisholm, F.A. Cotton and L.A. Rankel, J. Amer. Chem. Soc., 100 (1978) 5764.
8 M.D. Curtis, N.A. Fotinos, L. Messerle and A.P. Sattelberger, Inorg. Chem., 22 (1983) 1559.
9 M.J. McGlinchey, P. Bougeard, B.G. Sayer, R. Hofer and C.J.L. Lock, J. Chem. Soc., Chem. Commun., (1984) 789.
10 G. Hunter and K. Mislow, J. Chem. Soc., Chem. Commun., (1984) 172.
11 D.S. Ginley, C.R. Brock, M.S. Wrighton, B. Fischer, D.L. Tipton and R. Bau, J. Organomet. Chem., 157 (1978) 41.
12 M. Green, K. Marsden, I.D. Salter, F.G.A. Stone and P. Woodward, J. Chem. Soc., Chem. Commun., (1983) 446.
13 D.S. Ginley, C.R. Brock and M.S. Wrighton, Inorg. Chim. Acta, 23 (1977) 85.
14 R.M. Laine and P.C. Ford, J. Organomet. Chem., 124 (1977) 29.
15 F.Y. Petillon, F. Le Floch-Perennou, J.E. Guerchais, D.W.A. Sharp, L. Manojlovic-Muir, J. Organomet. Chem., 202 (1978) 23.
16 S.R. Finnimore, S.A.R. Knox and G.E. Taylor, J. Chem. Soc., Dalton Trans., (1982) 1783.
17 M. Green, S.J. Porter and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1983) 513.
18 C.P. Horwitz, E.M. Holt and D.F. Shriver, Inorg. Chem., 23 (1984) 2491.
19 R. Hoffmann, Angew. Chem. Int. Ed. Engl., 21 (1982) 711.
20 D.G. Evans, J. Chem. Soc., Chem. Commun., (1983) 676.
21 M.S. Wrighton and D.S. Ginley, J. Amer. Chem. Soc., 97 (1975) 4246.
22 P. Bougeard, B.D. Gupta and M.D. Johnson, J. Organomet. Chem., 206 (1980) 211.
23 D.D. Perrin and D.R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, New York, 1980.
24 R. Birdwhistell, P. Hackett and A.R. Manning, J. Organomet. Chem., 157 (1978) 239.
25 R.B. King, M.Z. Iqbal and A.D. King, J. Organomet. Chem., 171 (1979) 53.
26 A.I. Vogel, A Textbook of Practical Organic Chemistry, Longman, London, 1948.
27 G.A. Carriedo, J.A.K. Howard, D.B. Lewis, G.E. Lewis and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1985) 905.