Organometallics 1988, *7*, 319–325

Synthesis and Spectral Properties of $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$ and $[Mo(\mu\text{-}I)I(CO)(\eta^2\text{-}MeC_2Me)_2]_2$ Bis(alkyne) Complexes. X-ray Crystal Structures of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ and $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$

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Received May 12, 1987

Reaction of the complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) with 2 equiv of the alkyne ligands RC_2R' in CH_2Cl_2 at room temperature (R = R′ = Ph; R = Me, R′ = Ph; for M = W, R = R′ = Me, CH_2Cl, and *p*-Tol; R = Ph, R′ = CH_2OH) affords high yields of the new bis(alkyne) complexes $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$. The molybdenum complex $[MoI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ could not be isolated since it rapidly dimerizes with loss of acetonitrile to give the iodide-bridged dimer $[Mo(\mu\text{-}I)I(CO)(\eta^2\text{-}MeC_2Me)_2]_2$. The analogous tungsten compound is, however, inert to dimerization, even after being refluxed in $CHCl_3$ for 24 h. X-ray single crystallographic studies were carried out on the compounds $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me and Ph). Crystals of the former (R = Me) are triclinic of space group $P\bar{1}$, $Z = 2$, in a unit cell of dimensions $a = 7.282$ (8) Å, $b = 7.928$ (8) Å, $c = 15.894$ (13) Å, $\alpha = 71.8$ (1)°, $\beta = 100.7$ (1)°, and $\gamma = 87.7$ (1)°. Crystals of the latter are monoclinic of space group $I2/c$, $Z = 8$, in a unit cell of dimensions $a = 31.122$ (27) Å, $b = 10.470$ (9) Å, $c = 19.186$ (18) Å, and $\beta = 98.5$ (1)°. The structures have been refined to $R = 0.055$ (R = Me) and $R = 0.046$ (R = Ph) for 2422 and 3283 respective reflections above background. The coordination geometry about the tungsten in each is complex and may be considered to be octahedral, with, as expected, the alkyne ligands parallel to each other and trans to the two iodide ligands, leaving the carbon monoxide and acetonitrile ligands mutually trans. The ^{13}C NMR chemical shifts indicate that the alkyne ligands are donating a total of six electrons to the metal in these complexes.

Introduction

The unique ability of alkyne ligands to utilize their orthogonal metal dπ-orbitals in order to serve simultaneously as both good single-faced π-acceptors and good single-faced π-donors[1] has proved important in recent years. The ligand to metal π-donor potential of the filled alkyne perpendicular π-bonding component allows variable electron donor interactions that can range from two to four electrons depending on the complex under consideration.[2] There has been considerable interest in alkyne complexes of molybdenum(II) and tungsten(II) over the past 10 years or so, and a wide range of complexes containing cyclopentadienyl and dithiocarbamates as attached ligands, such as $[MX(CO)(\eta^2\text{-}PhC_2Ph)(\eta^5\text{-}C_5H_5)]$ (M = Mo or W; X = Cl, Br, or I),[3] $[M(CO)(S_2CNR_2)_2(\eta^2\text{-}RC_2R)]$ (M = Mo[4] or W;[5] R = alkyl or aryl), $[M(SR)(CO)(\eta^2\text{-}R'C_2R')(\eta^5\text{-}C_5H_5)]$ (R = CF_3 or C_6H_5; R′ = Me, CF_3 or Ph),[6] $[WMe(CO)(\eta^2\text{-}RC_2R)(\eta^5\text{-}C_5H_5)]$ (R = alkyl or aryl),[7] $[MoLL'(\eta^2\text{-}RC_2R')(\eta^5\text{-}C_5H_5)][BF_4]$ [L, L′ = CO and PR_3; L = L′ = $P(OMe)_3$; R, R′ = Me, Ph, etc.],[8] $[Mo(CO)L(\eta^2\text{-}RC_2R')(\eta^5\text{-}C_5H_5)][BF_4]$ (L = CO, $P(OPh)_3$, PEt_3, PPh_3; R = R′ = H, Me, Ph; R = H, R′ = Ph),[9] $[Mo(SR)[P(OMe)_3](\eta^2\text{-}MeC_2Me)(\eta^5\text{-}C_5H_5)]$ (R = Me, *p*-$NH_2C_6H_4$, *p*-$MeOC_6H_4$, *p*-MeC_6H_4, C_6H_5, or *p*-$NO_2C_6H_4$),[10] $[MX(\eta^2\text{-}RC_2R)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo, X = Cl, R = CH_2OH;[11] M = Mo or W; X = Cl, Br, or I; R = CF_3),[12] $[M(CO)(\eta^2\text{-}MeC_2Me)_2(\eta^5\text{-}C_5H_5)][PF_6]$ (M = Mo or W),[13] and $[Mo(S_2CNR_2)_2(\eta^2\text{-}RC_2R)_2]$,[14] has been reported. Some recent developments include the preparation of new halocarbonyl derivatives; in particular, Templeton and co-workers[15] have prepared $[MX_2(CO)L_2(\eta^2\text{-}RC_2R')]$ (M = Mo or W; X = Cl or Br; L = PPh_3, PEt_3, or py; $L_2 = Ph_2P(CH_2)_2PPh_2$] by reacting $[MX_2(CO)_nL_2]$ (n = 2 or 3) with free alkyne and Davidson and Vasapollo[16] treated $[W(\mu\text{-}Br)Br(CO)_4]_2$ with alkynes RC_2R' (R = R′ = Me, Et, or Ph) and PhC_2Me to give the dimeric alkyne compounds $[W(\mu\text{-}Br)Br(CO)(\eta^2\text{-}RC_2R')_2]_2$ which react with nucleophiles (L) to give the monoalkyne compounds $[WBr_2(CO)L_2(\eta^2\text{-}RC_2R')]$ [L =

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[1] Mingos, D. M. P. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds., Pergamon: Oxford, 1982; Vol. 3, pp 59–61.

[2] Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.

[3] Davidson, J. L.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* **1975**, 2531.

[4] McDonald, J. W.; Newton, W. E.; Creedy, C. T. C.; Corbin, J. L. *J. Organomet. Chem.* **1975**, *92*, C25.

[5] Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J.-J.; McDonald, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1318.

[6] Howard, J. A. K.; Stansfield, R. F. D.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1976**, 246.

[7] Alt, H. G. *J. Organomet. Chem.* **1977**, *127*, 349. (b) Alt, H. G.; Eichner, M. E.; Jansen, B. M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 861.

[8] Allen, S. R.; Baker, P. K.; Barnes, S. G.; Green, M.; Trollope, L.; Muir, L. M.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1981**, 873.

[9] Sünkel, K.; Nagel, U.; Beck, W. *J. Organomet. Chem.* **1981**, *222*, 251.

[10] Allen, S. R.; Glauert, T. H.; Green, M.; Mead, K. A.; Norman, N. C.; Orpen, A. G.; Shaverien, C. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2747.

[11] Faller, J. W.; Murray, H. H. *J. Organomet. Chem.* **1979**, *172*, 171.

[12] Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 738.

[13] Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 2698.

[14] Herrick, R. S.; Templeton, J. L. *Organometallics* **1982**, *1*, 842.

[15] (a) Winston, P. B.; Burgmayer, S. J. N.; Templeton, J. L. *Organometallics* **1983**, *2*, 167. (b) Winston, P. B.; Burgmayer, S. J. N.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1986**, *5*, 1707.

[16] (a) Davidson, J. L.; Vasapollo, G. *Polyhedron* **1983**, *2*, 305. (b) Davidson, J. L.; Vasapollo, G. *J. Chem. Soc., Dalton Trans.* **1985**, 2239.

0276-7333/88/2307-0319$01.50/0

CN-*t*-Bu, $P(OMe)_3$, or PPh_3; R = R′ = Me or Ph; R = Me, R′ = Ph]. Also Bennett and Boyd[17] prepared the cyclooctyne complexes $[MBr_2(CO)(PEt_3)_2(\eta^2\text{-}C_8H_{12})]$ (M = Mo or W) and very recently Mayr and co-workers[18] the alkylidene alkyne non-carbonyl-containing complex $[WCl_2(PMe_3)_2(\eta^1\text{-CPhH})(\eta^2\text{-PhC}_2\text{Ph})]$. Hitherto, the only diiodo carbonyl complexes of this type to be reported are $[WI_2(CO)_2L(\eta^2\text{-PhC}_2\text{H})]$ (L = PMe_3, $AsMe_3$, or CN-*t*-Bu) and $[WI_2(CO)_2L(\eta^2\text{-HC}_2\text{H}]$ (L = PMe_3 or $AsMe_3$) by Umland and Vahrenkamp.[19]

In recent years we have been investigating the chemistry of the highly versatile complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W).[20] In this paper we wish to report the syntheses of the new diiodo bis(alkyne) complexes $[MI_2(CO)(NCMe)(\eta^2\text{-RC}_2\text{R}')_2]$ (M = Mo or W; R = R′ = Ph; R = Me, R′ = Ph; for M = W, R = R′ = Me, CH_2Cl, and *p*-Tol; R = Ph, R′ = CH_2OH) and the iodide-bridged dimer $[Mo(\mu\text{-I})I(CO)(\eta^2\text{-MeC}_2\text{Me})_2]_2$.

Experimental Section

General Procedures. All manipulations were carried out under a nitrogen atmosphere by using standard Schlenk line techniques. Dichloromethane was dried over phosphorus pentoxide and purged with nitrogen before use. $[M(CO)_6]$ (M = Mo or W), acetonitrile, iodine, MeC_2Me, PhC_2Ph, PhC_2Me, $CH_2ClC_2CH_2Cl$, and *p*-$TolC_2$*p*-Tol were obtained from commercial sources. PhC_2CH_2OH was kindly donated by Professor C. J. M. Stirling, FRS (UCNW). The complexes $[MI_2(CO)_3(NCMe)_2]$ were prepared according to literature methods.[20]

^1H and ^{13}C NMR spectra were recorded either on a JEOL FX60 MHz or Bruker WH-400 MHz (at the University of Warwick) NMR spectrometer. All spectra were calibrated against tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 197 infrared spectrophotometer. Elemental analyses for carbon, hydrogen, and nitrogen were recorded on a Carlo Erba Elemental Analyser MOD 1106 (using helium as a carrier gas). The molecular Weight of 1 was measured by Rast's method[21] using camphor as the solvent. Magnetic susceptibility measurements were determined by using a Johnson-Matthey magnetic susceptibility balance.

Syntheses. $[Mo(\mu\text{-I})I(CO)(\eta^2\text{-MeC}_2\text{Me})_2]_2$ (1). To a solution of $[MoI_2(CO)_3(NCMe)_2]$ (0.362 g, 0.70 mmol) in 10 mL of CH_2Cl_2 at 0 °C in a foil-covered Schlenk tube was added 2-butyne (0.11 mL, 0.076 g, 1.41 mmol). The reaction was allowed to warm to room temperature and filtered after 17 h. The solvent was removed in vacuo and afforded a brown crystalline material, which was recrystallized from CH_2Cl_2. Yield: 0.265 g, 78%.

$[MoI_2(CO)(NCMe)(\eta^2\text{-MeC}_2\text{Ph})_2]$ (2). To a stirred solution of $[MoI_2(CO)_3(NCMe)_2]$ (0.511 g, 0.991 mmol) in dichloromethane (15 cm^3) in a foil-covered Schlenk tube cooled to 0 °C was added 1-phenyl-1-propyne (0.230 g, 1.982 mmol). The solution was slowly allowed to return to room temperature. Filtration and removal of solvent in vacuo gave a dark red crystalline powder, which was recrystallized from dichloromethane, giving pure $[MoI_2(CO)(NCMe)(\eta^2\text{-MeC}_2\text{Ph})_2]$. Yield: 0.52 g, 81%.

$[MoI_2(CO)(NCMe)(\eta^2\text{-PhC}_2\text{Ph})_2]$ (3) was prepared by an analogous procedure.

$[WI_2(CO)(NCMe)(\eta^2\text{-MeC}_2\text{Me})_2]$ (4). To a solution of $[WI_2(CO)_3(NCMe)_2]$ (0.50 g, 0.83 mmol) in 12 mL of CH_2Cl_2 at 0 °C was added 2-butyne (0.2 mL, 0.14 g, 2.56 mmol). The solution was allowed to return to room temperature after 2 h and was filtered after a further 15 h. The solvent was removed in vacuo to give a yellow powder that was dissolved in the minimum quantity of CH_2Cl_2. A few drops of Et_2O were added, and the solution was cooled to −18 °C for 17 h to give analytically pure yellow crystals. Yield: 0.463 g, 91%. The complex decomposes between 167 and 169 °C.

$[WI_2(CO)(NCMe)(\eta^2\text{-RC}_2\text{R}')_2]$ [R = Me, R′ = Ph (5), R = R′ = Ph (6), CH_2Cl (8), and *p*-Tol (9); R = Ph, R′ = CH_2OH (7)]. All five compounds were prepared by analogous procedures. The synthesis of 6 resulted from the addition of diphenylacetylene (0.295 g, 1.66 mmol) to an ice-cooled solution of $[WI_2(CO)_3(NCMe)_2]$ (0.500 g, 0.83 mmol) in 12 mL of CH_2Cl_2. The solution was allowed to return to room temperature immediately and was filtered after 17 h. The solvent was removed in vacuo to give an orange-yellow crystalline complex, which when dissolved in the minimum volume of CH_2Cl_2 and cooled to −18 °C afforded orange-yellow crystals. Yield: 0.67 g, 94%. The complex decomposes between 149 and 152 °C.

Crystal Data. 4: $WI_2C_{11}H_{15}NO\cdot 0.5CH_2Cl_2$; M_r 654.3; triclinic, space group $P\bar{1}$; $a = 7.282$ (8) Å, $b = 7.928$ (8) Å, $c = 15.894$ (13) A, $\alpha = 71.8$ (1); $\beta = 100.7$ (1)°, $\gamma = 87.7$ (1)°; $U = 852.1$ Å^3; D(calcd) = 2.54 g cm^{-3}, D(measd) = 2.52 g cm^{-3}, λ(Mo Kα) = 0.7107 Å; μ = 109.7 cm^{-1}; $F(000) = 588$. 6: $WI_2C_{31}H_{23}NO\cdot 0.5CH_2Cl_2$; M_r 942.1; monoclinic, space group $I2/c$; $a = 31.122$ (27) Å, $b = 10.470$ (9) Å, $c = 19.186$ (18) Å, $\beta = 98.5$ (1)°; $U = 6183.2$ Å^3; D(calcd) = 1.94 g cm^{-3}, D(measd) = 1.90 g cm^{-3}; λ(Mo Kα) = 0.7107 Å; μ = 60.82 cm^{-1}; $F(000) = 3400$.

Needle crystals of approximate size 0.4 × 0.3 × 0.2 mm (4) and 0.4 × 0.2 × 0.2 mm (6) were in turn mounted along the *a* axis of a Stoe STADI-2 diffractometer equipped with a graphite monochromator. Intensity data were measured by ω scans with a speed of 0.0333° s^{-1} and a background count of 20 s. A total of 2910 (4) and 6275 (6) independent reflections were measured with $2\theta < 50°$. Of these intensity data 2422 (4) and 3283 (6), all with $I > 3\sigma(I)$, were used in subsequent calculations. An empirical absorption factor[22] was applied to each set of data. Corrections of 0.75–1.35 for 4 and 0.63–1.26 for 6 were applied. Structures were determined by normal heavy-atom methods. Non-hydrogen atoms were refined anisotropically. H atoms were fixed in trigonal or tetrahedral positions at 0.95 Å from the C atoms to which they were bonded. Methyl hydrogen atoms were refined as rigid groups. In both structures a disordered solvent dichloromethane molecule was located and refined with an occupancy of 50%. Calculations were carried out with Shelx76[23] and some of our own programs on the Amdahl V7 at the University of Reading.

Final *R* values were 0.055 (R_w = 0.064) in 4, and 0.046 (R_w = 0.052) in 6. For both refinements (on *F*) the weighting scheme was chosen as $\omega = 1/(\sigma^2(F) + 0.002F^2)$ where $\sigma(F)$ was taken from counting statistics. This gave similar values of $\omega\Delta^2$ over ranges of $(\sin\theta)/\lambda$ and F_o. In final cycles of refinement no $\Delta/\sigma > 0.1$. Difference Fourier maps showed no significant peaks. Atomic coordinates for 4 and 6 are given in Tables V and VI. Molecular dimensions in the metal coordination spheres are given in Table VII. Remaining dimensions, thermal parameters, hydrogen positions, and structure factor tables are deposited in the supplementary material.

Results and Discussion

Syntheses. The $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) starting materials are synthesized by allowing the zerovalent compounds $[M(CO)_3(NCMe)_3]$ to react with I_2 at 0 °C to afford quantitative yields of the seven-coordinate compounds.[20] Reactions of the complexes $[MI_2(CO)_3(NCMe)_2]$ with 2 equivalents of RC_2R' in CH_2Cl_2 give high yields of the new alkyne complexes $[MI_2(CO)(NCMe)(\eta^2\text{-RC}_2\text{R}')_2]$ (M = Mo or W; R = R′ = Ph; R = Me, R′ = Ph; for M = W, R = R′ = Me, CH_2Cl, or *p*-Tol; R = Ph, R′ = CH_2OH). Reaction of $[MoI_2(CO)_3(NCMe)_2]$ with 2 equiv of but-2-yne at 0 °C rapidly affords the monoacetonitrile complex $[MoI_2(CO)(NCMe)(\eta^2\text{-MeC}_2\text{Me})_2]$ which could not be isolated in a pure state. The complex $[MoI_2(CO)(NCMe)(\eta^2\text{-MeC}_2\text{Me})_2]$ loses acetonitrile to give

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[17] Bennett, M. A.; Boyd, I. W. *J. Organomet. Chem.* **1985**, *290*, 165.

[18] Mayr, A.; Lee, K. S.; Kjelsberg, M. A.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 6079.

[19] Umland, P.; Vahrenkamp, H. *Chem. Ber.* **1982**, *115*, 3580.

[20] Baker, P. K.; Fraser, S. G.; Keys, E. M. *J. Organomet. Chem.* **1986**, *309*, 319.

[21] Mann, F. G.; Saunders, B. C. *Practical Organic Chemistry*; Longmans Green and Co: New York, 1954; pp 342–344.

[22] Walker, N.; Stuart, D. *Acta Crystallogr., Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1983**, *A39*, 158.

[23] Sheldrick, G. M. Shelx76, Package for Crystal Structure Determinations; University of Cambridge, Cambridge, U.K., 1976.

Table I. Physical and Analytical[a] Data for the Complexes $\mathrm{[Mo(\mu\text{-}I)I(CO)(\eta^2\text{-}MeC_2Me)_2]_2}$ and $\mathrm{[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]}$

complex	color	yield, % (pure product)	C	H	N
$\mathrm{[Mo(\mu\text{-}I)I(CO)(\eta^2\text{-}MeC_2Me)_2]_2}$ (1)	brown	78	21.8 (21.6)	2.5 (2.5)	
$\mathrm{[MoI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Ph)_2]}$ (2)	dark red	81	39.1 (38.7)	3.1 (2.9)	1.8 (2.2)
$\mathrm{[MoI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]}$ (3)	dark maroon	72	47.6 (48.1)	3.1 (3.0)	1.5 (1.8)
$\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]}$ (4)	yellow	91	21.3 (21.5)	2.5 (2.5)	2.8 (2.7)
$\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Ph)_2]}$ (5)	yellow	75	34.6 (34.1)	2.8 (2.6)	1.7 (1.9)
$\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]}$ (6)	deep yellow	94	43.0 (43.1)	2.9 (2.7)	1.7 (1.6)
$\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2CH_2OH)_2]}$ (7)	yellow	83	32.9 (32.7)	2.6 (2.5)	1.8 (1.8)
$\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}CH_2ClC_2CH_2Cl)_2]}$ (8)	pale green	62	17.5 (17.6)	2.0 (1.5)	1.6 (1.9)
$\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}}p\mathrm{\text{-}TolC_2}p\mathrm{\text{-}Tol)_2]}$ (9)	yellow	86	45.7 (45.5)	3.4 (3.4)	1.4 (1.5)

[a] Calculated values in parentheses.

Table II. IR Data[a] for the Complexes $\mathrm{[Mo(\mu\text{-}I)I(CO)(\eta^2\text{-}MeC_2Me)_2]_2}$ and $\mathrm{[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]}$

complex	ν(CO)/cm^{-1}	ν(C≡N)/cm^{-1}	ν(C≡C)/cm^{-1}
$\mathrm{[Mo(\mu\text{-}I)I(CO)(\eta^2\text{-}MeC_2Me)_2]_2}$ (1)	2010 (s), 1960 (s)		1610 (vw)
$\mathrm{[MoI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Ph)_2]}$ (2)	2075 (s)	2320, 2295 (w)	1610 (vw)
$\mathrm{[MoI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]}$ (3)	2090 (s)	2315, 2295 (w)	1605 (w)
$\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]}$ (4)	2050 (s)	2325, 2298 (w)	1642 (w)
$\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Ph)_2]}$ (5)	2080 (s)	2320, 2290 (w)	1643 (w)
$\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]}$ (6)	2090 (s)	2320, 2300 (w)	1618 (vw)
$\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2CH_2OH)_2]}$ (7)	2080 (s)	2325, 2300 (w)	1640 (vw)
$\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}CH_2ClC_2CH_2Cl)_2]}$ (8)	2100 (s)	2320, 2298 (w)	1643 (w)
$\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}}p\mathrm{\text{-}TolC_2}p\mathrm{\text{-}Tol)_2]}$ (9)	2095 (s)	2320, 2298 (w)	1638 (vw)

[a] Spectra run in $\mathrm{CHCl_3}$; NaCl plates. Abbreviations: s, strong; w, weak; vw, very weak.

the iodide-bridged dimer $\mathrm{[Mo(\mu\text{-}I)I(CO)(\eta^2\text{-}MeC_2Me)_2]_2}$. All of the complexes (1–9) have been fully characterized by elemental analysis (C, H, and N) (Table I), IR (Table II), and ^{1}H and ^{13}C NMR spectroscopy (Tables III and IV). In addition, molecular weight and magnetic susceptibility measurements confirm the dinuclear nature of the dimer $\mathrm{[Mo(\mu\text{-}I)I(CO)(\eta^2\text{-}MeC_2Me)_2]_2}$.

All of the complexes (1–9) are soluble in $\mathrm{CHCl_3}$ and $\mathrm{CH_2Cl_2}$ but only partially soluble in $\mathrm{Et_2O}$ and hydrocarbon solvents. The molybdenum complexes $\mathrm{[MoI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]}$ and $\mathrm{[Mo(\mu\text{-}I)I(CO)(\eta^2\text{-}MeC_2Me)_2]_2}$ are extemely unstable. Therefore it was difficult to get good analytical data for these complexes despite many attempted preparations and recrystallizations. However the tungsten analogues, in particular $\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]}$ (R = Me or Ph), are very stable. Although the complexes $\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]}$ (R = Me or Ph), which have been structurally characterized by X-ray crystallography, contain dichloromethane of solvation, many subsequent preparations of these compounds do not show solvated $\mathrm{CH_2Cl_2}$ from ^{1}H NMR and microanalysis.

The molybdenum complex $\mathrm{[MoI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]}$, which rapidly dimerizes with loss of acetonitrile to give an iodide-bridged dimer, is analogous to the bromide-bridged dimers $\mathrm{[W(\mu\text{-}Br)Br(CO)(\eta^2\text{-}RC_2R')_2]_2}$ (R = R′ = Me, Et, or Ph; R = Me, R′ = Ph), reported by Davidson and Vasapollo.[16] Similar treatment of $\mathrm{[MoI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]}$ (R = Ph, R′ = Ph or Me) did not yield dimeric products, even when heated to reflux in $\mathrm{CH_2Cl_2}$ for 24 h. However no organometallic products could be isolated from the above reactions. The tungsten complexes 4 and 6 are also inert to dimerization, and analytically pure $\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]}$ (R = Me or Ph) complexes are isolated from solutions of the monomeric bis(alkyne) complexes which have been boiled under reflux in $\mathrm{CHCl_3}$ for 24 h.

The greater ease of dimerization with loss of acetonitrile of molybdenum(II) compared to tungsten(II) has been previously observed with the seven-coordinate complexes $\mathrm{[MI_2(CO)_3(NCMe)L]}$ (L = phosporus, arsenic, and antimony donor ligands).[24]

Table III. ^{1}H NMR Data[a] for the Complexes $\mathrm{[Mo(\mu\text{-}I)I(CO)(\eta^2\text{-}MeC_2Me)_2]_2}$ and $\mathrm{[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]}$

complex	^{1}H (δ)
$\mathrm{[Mo(\mu\text{-}I)I(CO)(\eta^2\text{-}MeC_2Me)_2]_2}$ (1)	2.99, 2.93 (s, 12 H, *Me*C$_2$); 2.33 (s, 12 H, C$_2$*Me*)
$\mathrm{[MoI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Ph)_2]}$ (2)	7.53 (m, 10 H, PhC$_2$); 2.26 (s, 6 H, *Me*C$_2$); 2.04 (s, 3 H, NC*Me*)
$\mathrm{[MoI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]}$ (3)	7.44 (m, 20 H, *Ph*C$_2$); 7.48 (br s, 3 H, NC*Me*)
$\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]}$[a] (4)	2.92 (s, 3 H, NC*Me*); 2.87 (d, 6 H, *Me*C$_2$); 2.79 (d, 6 H, C$_2$*Me*)
$\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Ph)_2]}$ (5)	7.35 (m, 10 H, *Ph*C$_2$); 3.12 (s, 6 H, *Me*C$_2$); 2.52 (s, 3 H, NC*Me*)
$\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]}$[a] (6)	7.5 (m, 20 H, *Ph*C$_2$); 2.35 (s, 3 H, NC*Me*)
$\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2CH_2OH)_2]}$ (7)	7.35 (m, 10 H, *Ph*C$_2$); 4.5 (s, 4 H, C$_2$C*H*$_2$O); 2.17 (br s, 2 H, O*H*); 2.01 (s, 3 H, NC*Me*)
$\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}CH_2ClC_2CH_2Cl)_2]}$ (8)	4.53 (m, 8 H, CH$_2$ClC$_2$); 2.88 (s, 3 H, NC*Me*)
$\mathrm{[WI_2(CO)(NCMe)(\eta^2\text{-}}p\mathrm{\text{-}TolC_2}p\mathrm{\text{-}Tol)_2]}$ (9)	7.38 (m, 10 H, *Ph*C$_2$); 2.79 (s, 6 H, C$_2$*Me*); 2.59 (s, 3 H, NC*Me*)

[a] Spectra recorded in $\mathrm{CD_2Cl_2}$ on the Bruker WH 400 instrument at Warwick. All other spectra recorded in $\mathrm{CDCl_3}$ on a JEOL FX60 NMR spectrometer. Abbreviations: m, multiplet; s, singlet; br, broad.

Infrared studies indicate that the reactions proceed via the iodide-bridged dimers $\mathrm{[M(\mu\text{-}I)I(CO)(NCMe)(\eta^2\text{-}RC_2R')]_2}$, which have been isolated and fully characterised.[25] For example, the reaction of $\mathrm{[WI_2(CO)_3(NCMe)_2]}$

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(24) Baker, P. K.; Fraser, S. G. *Polyhedron* **1986**, *5*, 1381.

(25) Baker, P. K.; Keys, E. M. *Polyhedron* **1986**, *5*, 1233.

Table IV. Selected ^{13}C NMR Spectra[a] of $[Mo(\mu\text{-}I)I(CO)(\eta^2\text{-}MeC_2Me)_2]_2$ and $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$

complex	^{13}C (δ)
$[Mo(\mu\text{-}I)I(CO)(\eta^2\text{-}MeC_2Me)_2]_2$ (1)	222.17 (CO); 194.34 ($C{\equiv}C$); 43.92, 29.63 (MeC_2Me)
$[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$[a] (4)	206.84 (CO); 167.69, 156.69 ($MeC{\equiv}CMe$); 128.65 ($N{\equiv}CMe$); 19.71, 15.78 (MeC_2Me); 4.71 ($NCMe$)
$[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Ph)_2]$ (5)	199.08 (CO); 164.38, 158.54 ($C{\equiv}C$); 133.33, 131.25 (PhC_2Ph); 125.14 (*o*-Ph); 124.23 (*m*-Ph); 123.45 (*p*-Ph); 115.45 ($N{\equiv}CMe$); 16.63, 13.38 (MeC_2Me); 4.55 ($NCMe$)
$[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$[a,b] (6)	201.28 (CO); 175.16, 163.98 ($C{\equiv}C$); 137.48, 135.49 (Ph); 130.03, 129.42 (*o*-Ph); 128.90, 128.71 (*m*-Ph); 127.93 (*p*-Ph); 4.33 ($NCMe$)
$[WI_2(CO)(NCMe)(\eta^2\text{-}CH_2ClC_2CH_2Cl)_2]$[a] (8)	195.63 (CO); 187.18, 179.61, ($C{\equiv}C$); 129.49 ($N{\equiv}C$); 25.51 (CH_2Cl); 5.62 ($NCMe$)

[a] Spectra recorded in CD_2Cl_2 on the Bruker WH 400 spectrometer at Warwick. All other spectra recorded in $CDCl_3$ on the JEOL FX60 spectrometer. [b] $N{\equiv}C$ not seen possibly due to being hidden under the phenyl peak.

Table V. Atomic Coordinates (×10^4) for 4 with Estimated Standard Deviations in Parentheses

atom	x	y	z
W(1)	928 (1)	3012 (1)	2661.5 (4)
I(1)	3301 (2)	3450 (2)	4197 (1)
I(2)	2407 (2)	6162 (2)	1699 (1)
N(1)	−902 (21)	4911 (20)	2893 (9)
C(2)	−1798 (24)	5879 (25)	3030 (10)
C(3)	−3009 (30)	7086 (35)	3213 (19)
C(51)	1842 (32)	−1434 (22)	3699 (13)
C(5)	884 (21)	325 (20)	3418 (20)
C(6)	−348 (27)	1248 (23)	3533 (12)
C(61)	−1857 (28)	1270 (24)	4002 (12)
C(91)	897 (36)	1733 (33)	817 (13)
C(9)	181 (22)	2491 (21)	1420 (10)
C(10)	−1111 (25)	3469 (22)	1527 (10)
C(101)	−2954 (29)	4364 (30)	1066 (14)
C(12)	3124 (23)	1746 (21)	2524 (11)
O(13)	4350 (17)	1062 (20)	2460 (9)
Cl(1)[a]	7140 (32)	−689 (28)	875 (13)
C(100)[a]	5403 (111)	510 (100)	269 (51)
Cl(2)[a]	4143 (42)	−88 (36)	−649 (17)

[a] Refined with 50% occupancy.

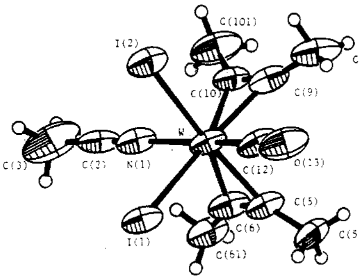

Figure 1. The structure of 4. Ellipsoids are shown at 50% probability.

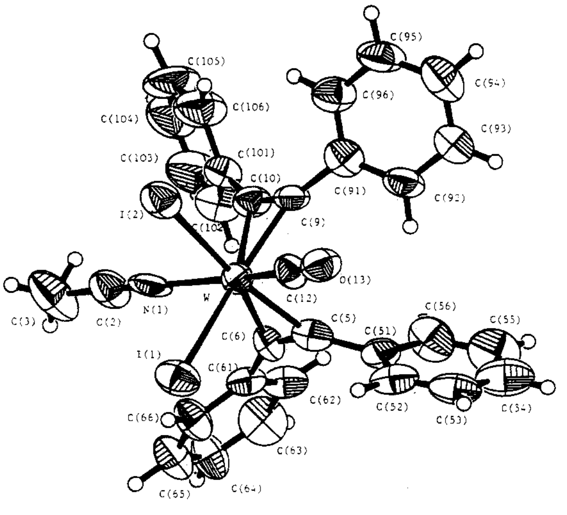

Figure 2. The structure of 6. Ellipsoids are shown at 50% probability.

Table VI. Atomic Coordinates (×10^4) for 6 with Estimated Standard Deviations in Parentheses

atom	x	y	z
W(1)	1311.1 (2)	1091 (1)	3139.8 (4)
I(1)	790.7 (4)	2708 (1)	2162 (1)
I(2)	1227.7 (4)	−667 (1)	1985 (1)
C(6)	1205 (4)	2306 (17)	3938 (8)
C(61)	874 (5)	2641 (16)	4366 (9)
C(62)	1007 (6)	2765 (18)	5106 (9)
C(63)	682 (7)	3128 (25)	5493 (11)
C(64)	269 (5)	3364 (22)	5226 (11)
C(65)	143 (5)	3301 (22)	4495 (11)
C(66)	450 (4)	2928 (21)	4102 (10)
C(5)	1557 (5)	2655 (17)	3727 (8)
C(51)	1927 (5)	3573 (15)	3861 (10)
C(52)	2026 (7)	4370 (18)	3343 (11)
C(53)	2383 (7)	5089 (20)	3416 (10)
C(54)	2639 (8)	5115 (26)	4081 (13)
C(55)	2556 (8)	4356 (26)	4588 (15)
C(56)	2195 (7)	3573 (24)	4482 (10)
C(10)	1526 (5)	−417 (17)	3784 (10)
C(9)	1850 (5)	−11 (16)	3535 (9)
C(101)	1350 (5)	−1395 (17)	4213 (10)
C(102)	1134 (6)	−1054 (22)	4771 (10)
C(103)	1007 (8)	−1977 (30)	5150 (17)
C(104)	1024 (7)	−3184 (29)	5058 (16)
C(105)	1220 (9)	−3600 (21)	4480 (19)
C(106)	1405 (7)	−2698 (24)	4049 (17)
C(91)	2317 (5)	−242 (19)	3525 (9)
C(92)	2612 (5)	726 (18)	3639 (10)
C(93)	3048 (6)	490 (23)	3661 (12)
C(94)	3183 (6)	−742 (26)	3516 (13)
C(95)	2875 (6)	−1664 (22)	3355 (13)
C(96)	2450 (6)	−1434 (19)	3403 (11)
N(1)	687 (4)	338 (13)	3319 (9)
C(2)	387 (5)	−21 (21)	3470 (11)
C(3)	−29 (7)	−481 (32)	3639 (17)
C(12)	1786 (5)	1682 (18)	2604 (9)
O(13)	2056 (3)	1960 (12)	2293 (7)
Cl(1)[a]	4558 (8)	1574 (27)	7551 (15)
Cl(2)[a]	5397 (12)	1276 (31)	8022 (19)
C(32)	5000[b]	479 (70)	7500[b]

[a] Refined with 50% occupancy. [b] Parameter fixed.

with 2 equiv of PhC_2Ph has been followed by infrared spectroscopy. The infrared spectrum ($CHCl_3$) of the reaction mixture after 5 min shows a strong carbonyl band at 1948 cm^{-1} due to the mononuclear complex $[WI_2(CO)(NCMe)_2(\eta^2\text{-}PhC_2Ph)]$ and also two higher carbonyl bands at 2050 and 1995 cm^{-1} due to the iodide-bridged dimer $[W(\mu\text{-}I)I(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)]_2$. The band at 1948 cm^{-1} disappears after 2 h, and a new band at 2090 cm^{-1} is observed due to the bis(alkyne) complex $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ (**6**). The carbonyl bands due to the dimeric complex $[W(\mu\text{-}I)I(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)]_2$ have completely disappeared after 4 h, leaving only the band at 2090 cm^{-1} due to **6**. The dinuclear complexes $[M(\mu\text{-}I)I(CO)(NCMe)(\eta^2\text{-}RC_2R')]_2$ react with RC_2R' to give the compounds $[MI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$ via symmetrical cleavage of the iodide bridges. The formation of the molybdenum bis(but-2-yne) dimer $[Mo(\mu\text{-}I)I\text{-}$

$(CO)(\eta^2\text{-}MeC_2Me)_2]_2$ probably proceeds with loss of acetonitrile from $[MoI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ to give the five-coordinate intermediate $[MoI_2(CO)(\eta^2\text{-}MeC_2Me)_2]$ since analogues of the five-coordinate intermediates $[WBr_2(CO)(\eta^2\text{-}CF_3C_2CF_3)_2]$[26] and $[Mo(S\text{-}t\text{-}Bu)_2(CN\text{-}t\text{-}Bu)_2(\eta^2\text{-}RC_2R')]$ (R, R′ = H or Ph)[27] have been previously reported. Dimerization can occur by attack of iodide lone pairs into the vacant coordination site. The structures of the mononuclear complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me and Ph) have been determined by X-ray crystallography.

Discussion of the Structures. The two structures are shown in Figures 1 and 2. In both molecules the tungsten atoms are eight-coordinate, being bonded to two iodine atoms, one carbonyl group, one acetonitrile group, and two alkyne ligands. The geometry of the two coordination spheres are similar, but there are a few significant differences.

While the formal geometry of the metal atom is eight-coordinate, it is convenient to describe the geometry as six-coordinate with the alkyne ligands each occupying one coordination site. The two iodine atoms are mutally cis and each is trans to an alkyne group. The carbonyl group is trans to the acetonitrile group.

The geometry of the WI_2 moieties is equivalent in the two structures with W–I bond lengths 2.843 (1) and 2.859 (1) Å in **4** and 2.848 (1) and 2.862 (2) Å in **6** and internal angles of 83.5 (1) and 84.0 (1)°, respectively.

In **4** the W(1)–C(5) and W(1)–C(9) bonds at 2.099 (15) and 2.119 (15) Å, respectively, are significantly longer than W(1)–C(6) and W(1)–C(10) bonds at 2.027 (18) and 2.037 (14) Å, respectively. We ascribe this to steric effects as C(5) and C(9) have equivalent positions in the coordination sphere both being cis to C(12) of the carbonyl group.

By contrast in **6** the difference is much less with the W(1)–C(5) and W(1)–C(9) bonds at [2.070 (16), 2.083 (15) Å] only slightly longer than W(1)–C(6) and W(1)–C(9) [2.056 (17), 2.083 (15) Å]. It is perhaps significant that in this structure C(12) is displaced further away from C(5) and C(9) presumably because of the steric effects of the phenyl rings. Indeed an analysis of the angles subtended at the metal atoms in the two structures (Table VII) shows that the only angle variations that are >2.4° involve C(12). In **6** C(12) is closer to the iodine atoms [I–W–C(12) decreases from 85.9 (5) and 85.1 (5)° in **4** to 82.5 (5) and 78.2 (5)° in **6**] and further away from C(5) and C(9) [C–W–C(12) being 74.3 (6) and 73.3 (6)° in **4** and 78.2 (6) and 75.2 (6)° in **6**]. Thus it would appear that because C(12) is further away in **6** from the bulky alkynes, it does not cause as much asymmetry in the W–C(alkyne) bond lengths. Although the W–C(12) bond length in **6** is much longer at 2.018 (17) Å than in **4** [1.937 (14) Å], this is not significant as the W···O distances are comparable and presumably the positions of the carbon atoms in the carbonyl groups are subject to the usual error. However the W(1)–N(1) bond length is also slightly longer in **6** than in **4**.

Details of least-squares calculations are shown in Table VIII. The angle between the W,C(5),C(6) and W,C(9),C(10) planes is 101.3 (1)° in **4** and 100.0 (1)° in **6**. The phenyl rings in **6** intersect the appropriate plane at similar angles ranging from 128.1 (1) to 119.1 (1)°.

The C(5)–C(6) and C(9)–C(10) distances are as expected being 1.21 (2) and 1.26 (2) Å, respectively, in **4** and 1.28 (2) and 1.25 (2) Å, respectively, in **6**. The C–C–C angles including these bonds are 145 (2), 145 (2), 147 (2), and 140 (2)° in **4** and 145 (2), 144 (2), 147 (2), and 143 (2)° in **6**.

Table VII. Molecular Dimensions in 4 and 6[a]

	4	6
(a) Metal Coordination Spheres		
W(1)–I(1)	2.843 (1)	2.848 (1)
W(1)–I(2)	2.859 (1)	2.862 (2)
W(1)–N(1)	2.132 (14)	2.169 (14)
W(1)–C(5)	2.099 (15)	2.070 (16)
W(1)–C(6)	2.027 (18)	2.056 (17)
W(1)–C(9)	2.119 (15)	2.083 (15)
W(1)–C(10)	2.037 (14)	2.054 (18)
W(1)–C(12)	1.937 (14)	2.018 (17)
I(1)–W(1)–I(2)	83.51 (4)	83.96 (4)
I(1)–W(1)–N(1)	81.7 (4)	83.4 (4)
I(2)–W(1)–N(1)	82.4 (4)	84.7 (4)
I(1)–W(1)–C(5)	88.7 (4)	91.0 (4)
I(2)–W(1)–C(5)	158.5 (4)	156.1 (5)
N(1)–W(1)–C(5)	116.4 (5)	118.0 (6)
I(1)–W(1)–C(6)	87.6 (5)	89.1 (4)
I(2)–W(1)–C(6)	163.5 (5)	165.6 (4)
N(1)–W(1)–C(6)	82.6 (6)	82.0 (5)
C(5)–W(1)–C(6)	34.1 (6)	36.1 (6)
I(1)–W(1)–C(9)	158.1 (4)	156.6 (5)
I(2)–W(1)–C(9)	87.8 (5)	84.4 (5)
N(1)–W(1)–C(9)	117.1 (5)	115.6 (5)
C(5)–W(1)–C(9)	92.1 (6)	91.5 (6)
C(6)–W(1)–C(9)	105.2 (6)	106.3 (9)
I(1)–W(1)–C(10)	162.2 (5)	162.9 (5)
I(2)–W(1)–C(10)	87.1 (5)	87.4 (5)
N(1)–W(1)–C(10)	82.0 (6)	81.1 (6)
C(5)–W(1)–C(10)	105.1 (6)	102.7 (6)
C(6)–W(1)–C(10)	97.5 (7)	95.8 (7)
C(9)–W(1)–C(10)	35.4 (6)	35.2 (6)
I(1)–W(1)–C(12)	85.9 (5)	82.5 (5)
I(2)–W(1)–C(12)	85.1 (5)	78.0 (5)
N(1)–W(1)–C(12)	163.3 (6)	158.7 (6)
C(5)–W(1)–C(12)	74.3 (6)	78.2 (6)
C(6)–W(1)–C(12)	108.2 (7)	113.6 (6)
C(9)–W(1)–C(12)	73.3 (6)	75.2 (6)
C(10)–W(1)–C(12)	108.4 (6)	110.1 (6)
(b) Further Dimensions		
N(1)–C(2)	1.09 (2)	1.09 (2)
C(2)–C(3)	1.41 (2)	1.46 (3)
C(51)–C(5)	1.43 (2)	1.49 (2)
C(5)–C(6)	1.21 (2)	1.28 (2)
C(6)–C(61)	1.44 (3)	1.45 (2)
C(91)–C(9)	1.44 (2)	1.48 (2)
C(9)–C(10)	1.26 (2)	1.25 (2)
C(10)–C(101)	1.44 (2)	1.47 (3)
C(12)–O(13)	1.06 (2)	1.14 (2)
W(1)–N(1)–C(2)	178.1 (13)	173.6 (16)
N(1)–C(2)–C(3)	177.8 (22)	177.0 (22)
W(1)–C(5)–C(51)	144.8 (13)	144.8 (12)
W(1)–C(5)–C(6)	69.7 (11)	71.3 (10)
C(51)–C(5)–C(6)	145.1 (18)	143.7 (16)
W(1)–C(6)–C(5)	76.2 (12)	72.6 (10)
W(1)–C(6)–C(61)	138.4 (13)	141.0 (11)
C(5)–C(6)–C(61)	145.4 (18)	145.5 (17)
W(1)–C(9)–C(91)	143.4 (13)	145.7 (13)
W(1)–C(9)–C(10)	68.8 (9)	71.2 (10)
C(91)–C(9)–C(10)	147.1 (16)	143.1 (17)
W(1)–C(10)–C(9)	75.9 (9)	73.7 (11)
W(1)–C(10)–C(101)	144.1 (13)	139.2 (11)
C(9)–C(10)–C(101)	140.0 (15)	146.9 (16)
W(1)–C(12)–O(13)	178.6 (15)	176.9 (16)

[a] Distances in Å and angles in deg. Dimensions of phenyl rings and solvent molecules are given in the supplementary material.

Plane 7 (see Table VIII) is calculated through W,I(1),I(2) and the midpoints of the two alkyne bonds. These five points are planar to within 0.07 Å in the two structures, and the deviations show that the alkyne bonds are approximately perpendicular to this plane. The tungsten is slightly out of this plane (0.05 Å in **4**, 0.07 Å in **6**) in a direction toward the acetonitrile, suggesting that the trans

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(26) Davidson, J. L.; Vasapollo, G.; Muir, L. M.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1982**, 1025.

(27) Kamata, M.; Yoshida, T.; Otsuka, S.; Hirotsu, K.; Higuchi, T.; Kido, M.; Tatsumi, K.; Hoffmann, R. *Organometallics* **1982**, *1*, 227.

Table VIII. Least-Squares Plane Calculations

Plane 1: W(1), C(5), C(6)
Plane 2: W(1), C(9), C(10)
Plane 3: C(51), C(52), C(53), C(54), C(55), C(56)
Plane 4: C(61), C(62), C(63), C(64), C(65), C(66)
Plane 5: C(91), C(92), C(93), C(94), C(95), C(96)
Plane 6: C(101), C(102), C(103), C(104), C(105), C(106)

Angles between the planes in 4	1 and 2	101.3 (1)°
Angles between the planes in 6	1 and 2	100.0 (1)°
	1 and 3	119.1 (1)°
	1 and 4	123.1 (1)°
	2 and 5	128.1 (1)°
	2 and 6	121.8 (1)°

Plane 7[a]

	deviation	
	4	6
W(1)	−0.05	−0.07
I(1)	0.00	−0.01
I(2)	0.01	0.02
N(1)*	−2.13	−2.20
C(5)*	0.63	0.68
C(6)*	−0.58	−0.58
C(9)*	0.64	0.62
C(10)*	−0.62	−0.63
C(12)*	1.88	1.90
M(5–6)[b]	0.02	0.05
M(9–10)[b]	0.01	−0.00

[a] Atoms not contributing to the plane are marked with an asterisk. Deviations from the plane in Å. [b] M(5–6) is the midpoint between C(5) and C(6), and M(9–10) is the midpoint between C(9) and C(10).

carbonyl group is more strongly bonded.

In neither molecule are there any intermolecular contacts less than the sum of van der Waals radii.

There are no comparable tungsten complexes. The closest analogue is dibromodicarbonyl(η^4-norbornadiene)tungsten(II), [$WBr_2(CO)_2(\eta^4$-nbd)],[28] in which the carbonyl groups are trans but the Br–W–Br angle is 109.9° and the diene groups are much closer to each other than in the present structures.

There are two possible types of structure of the dinuclear molybdenum complex [$Mo(\mu$-I)I(CO)(η^2-$MeC_2Me)_2]_2$ (1) either as an iodide-bridged dimer with one two-electron and one four-electron alkyne ligand or as a Mo=Mo iodide-bridged bonded dimer with both alkyne ligands donating two electrons to the metal center. Although a wide range of multiple-bonded complexes of molybdenum(II) are known,[29] it is highly unlikely that this complex has Mo=Mo double bonds. There is no precedent for molybdenum(II) complexes in which both alkyne ligands are two electron donors. ^{13}C NMR spectroscopy has shown that the two alkyne ligands are donating on average "three-electrons" each (see later in the paper). Although there are a wide range of possible isomers of the bis(alkyne) complex, the X-ray crystal structures of [WI_2(CO)(NCMe)(η^2-$RC_2R)_2$] (R = Me or Ph) described above suggest that the alkyne ligands will be cis and fac with a carbonyl ligand in accord with simple bonding arguments.[30] The most likely two possible geometrical isomers shown in parts a and b of Figure 3 are both supported by ^1H NMR measurements which show two different methyl resonances. It is highly likely that Figure 3a is the preferred geometry since the carbonyl infrared pattern indicates two closely spaced bands with similar intensity in accord with cis carbonyls having a small interaction between the ligands. This geometry is also suggested by Davidson and Vasapollo[16] for the bromide-bridged dimers [$W(\mu$-Br)Br(CO)(η^2-$RC_2R)_2]_2$ (R = Me, Et, or Ph).

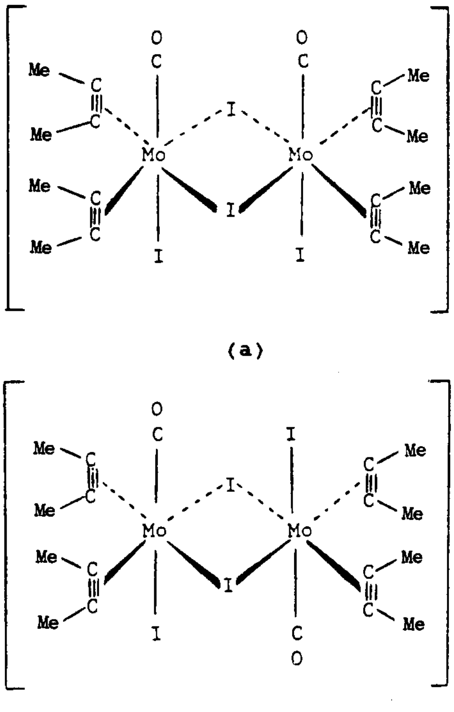

Figure 3. Proposed structures for [$Mo(\mu$-I)I(CO)(η^2-$MeC_2Me)_2]_2$.

Spectroscopic Studies. The infrared spectra (Table II) of the monomeric complexes [MI_2(CO)(NCMe)(η^2-$RC_2R')_2$] all show a single carbonyl resonance above 2000 cm^{-1}, which is very similar to the analogous cyclopentadienyl bis(alkyne) cations [Mo(CO)(η^2-$RC_2R)_2(\eta^5$-$C_5H_5)][BF_4]$ reported by Green and Bottrill.[31] It is interesting to note that the colors of the bis(butyne) complexes [WI_2(CO)(NCMe)(η^2-$MeC_2Me)_2$] (4) and [Mo(CO)(η^2-$MeC_2Me)_2(\eta^5$-$C_5H_5)][BF_4]$ are similar (pale yellow) and the analogous pair of diphenylacetylene complexes are dark yellow/orange and both sets of complexes also have two alkynes donating a total of six electrons to the metal. (P.K.B. has prepared the complexes [Mo(CO)(η^2-$RC_2R)_2(\eta^5$-$C_5H_5)][BF_4]$ (R = Me or Ph) many times).

The infrared spectra of the monomeric complexes also show asymmetric doublets at, for example, 2325 and 2298 cm^{-1} for 4 which can be assigned to coordinated acetonitrile. The increase in ν(CN) upon coordination to the metal can be attributed to coupling of the C–N bond to the N–metal stretching vibrations and to an increased C–N force constant which implies that the acetonitrile is functioning as a pure σ-donor ligand.[32] The alkyne (C≡C) stretching bands occur at ≃1620 cm^{-1} and, as expected, are much lower than for the uncoordinated alkyne owing to back-donation into empty π^*-antibonding orbitals of the alkyne upon coordination to the metal.

The room-temperature ^1H NMR spectra (Table III) show the expected resonances for the static structures

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(28) Cotton, F. A.; Meadows, J. H. *Inorg. Chem.* **1984,** *23,* 4688.

(29) Cotton, F. A.; Walton, R. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982 and references cited therein.

(30) (a) Braterman, P. S.; Davidson, J. L.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* **1976,** 241. (b) Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.* **1982,** 21, 466. (c) Templeton, J. L.; Winston, P. B.; Ward, B. C. *J. Am. Chem. Soc.* **1981,** *103,* 7713. (d) Kamata, M.; Hirotsu, K.; Higuchi, T.; Kido, M.; Tatsumi, T.; Yoshida, T.; Otsuka, S. *Inorg. Chem.* **1983,** *22,* 2416.

(31) Bottrill, M.; Green, M. *J. Chem. Soc., Dalton Trans.* **1977,** 2365.

(32) Ford, P. C.; Clarke, R. E. *J. Chem. Soc., Chem. Commun.* **1968,** 1109.

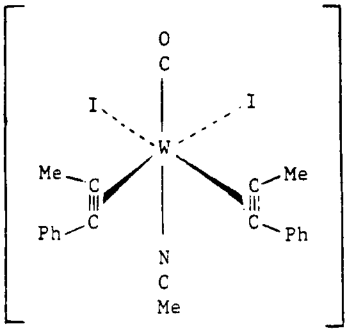

Figure 4. Proposed structure of $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Me)_2]$.

indicated in Figures 1–3. All of the RC_2R type complexes show two sets of R group resonances due to being cis to either carbon monoxide or acetonitrile, except for the bis(*p*-tolyl) complex **9** which shows only one methyl resonance, thus indicating that the methyl groups are too far away from the metal to be affected by other groups coordinated to the metal. All of the other bis PhC_2R complexes show only one R′ resonance indicating that one isomer predominates in these complexes, in accord with infrared spectroscopy. For example, **5** has one C≡CMe resonance at δ −3.12, and it would appear from the crystal structures of **4** and **6** the bond angle involving the group nearest to carbon monoxide is much less and hence on steric grounds it is likely that the methyl groups will be *cis* to the carbon monoxide ligand as shown in Figure 4.

The ^{13}C NMR spectra of both monomeric and dimeric complexes discussed in this paper show alkyne carbon resonances between 194 and 157 ppm which indicates that the alkynes are bonding as rapidly equilibrating 2- and 4-electron donors, each donating an average of three electrons to the metal center. This would allow the complexes to obey the effective atomic number rule which is highly likely because of the diamagnetism of the complexes. Templeton and Ward[2] reported the number of electrons donated by an alkyne can be correlated with the ^{13}C chemical shifts of the coordinated alkyne carbon atoms. The alkyne carbon ^{13}C shifts of complexes **1**–**9** agrees with the alkynes donating an average of three electrons each to the metal.

Acknowledgment. We thank the SERC for support. We also thank Dr. O. W. Howarth (University of Warwick) for running ^1H and ^{13}C NMR spectra.

Registry No. **1**, 111112-42-6; **2**, 111187-46-3; **3**, 111187-47-4; **4**, 111187-48-5; **5**, 111187-49-6; **6**, 111187-50-9; **7**, 111112-43-7; **8**, 111112-44-8; **9**, 111112-45-9; $[MoI_2(CO)_3(NCMe)_2]$, 102349-56-4; $[Wi_2(CO)_3(NCMe)_2]$, 102382-37-6; MeC_2Me, 503-17-3; MeC_2Ph, 673-32-5; PhC_2Ph, 501-65-5; PhC_2CH_2OH, 1504-58-1; $CH_2ClC_2CH_2Cl$, 821-10-3; *p*-tolC_2*p*-tol, 2789-88-0.

Supplementary Material Available: Tables of remaining dimensions, hydrogen coordinates, and anisotropic thermal parameters in **4** and **6** (8 pages); listings of structure factors (25 pages). Ordering information is given on any current masthead page.

Metal Carbonyl Syntheses. 18.[1] Hydrogen-Bridged Heterobimetallic Complexes: Structural Characterization of $(\eta\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}H)Cr(CO)_5$, $[((\eta\text{-}C_5H_5)_2(CO)Nb)_2(\mu\text{-}H)]^+[Mn(CO)_5]^-$, and $(\eta\text{-}C_5H_5)_2(CO)Ta(\mu\text{-}H)Mn_2(CO)_9$

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Received June 1, 1987

Three examples of complexes from the general class $(\eta\text{-}C_5H_5)_2(CO)M(\mu\text{-}H)M'L_n$, where M = Nb or Ta and $M'L_n$ is a 16-electron fragment, have been structurally characterized. Crystal data for $(\eta\text{-}C_5H_5)_2(CO)Nb(\mu\text{-}H)Cr(CO)_5$ (**1a**): monoclinic; space group $P2_1/n$; $a = 919.5$ (3), $b = 1426.4$ (6), $c = 1316.0$ (3) pm; $\beta = 103.44$ (3)°; $Z = 4$; final $R = 0.077$ for 2766 reflections used. Crystal data for $[((\eta\text{-}C_5H_5)_2(CO)Nb)_2(\mu\text{-}H)]^+[Mn(CO)_5]^-$ (**2a**): orthorhombic; space group $P2_12_12_1$; $a = 1358.3$ (3), $b = 1556.5$ (4), $c = 1262.2$ (2) pm; $Z = 8$; final $R = 0.045$ for 3565 reflections used. Crystal data for $(\eta\text{-}C_5H_5)_2(CO)Ta(\mu\text{-}H)Mn_2(CO)_9$ (**3b**): monoclinic; space group $P2_1/a$; $a = 1487.2$ (3), $b = 1075.6$ (2), $c = 1559.1$ (3) pm; $\beta = 114.04$ (1)°; $Z = 4$; final $R = 0.052$ for 4469 reflections used. Comparison of structural parameters among these and related complexes indicates all members of this class can be viewed as containing three-center, two-electron M–H–M′ bonds, with the 18-electron $(\eta\text{-}C_5H_5)_2(CO)M\text{–}H$ grouping effectively acting as a two-electron donor to the coordinatively unsaturated $M'L_n$ fragment.

Introduction

While interest in metal–metal bonded organotransition metal complexes has never been lacking, in recent years there has been particular activity aimed at synthesis and characterization of heterobimetallic complexes. There are a number of reasons for this attention;[4] prominent among them is the idea that a complex combining an early and

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(1) Part 17: Hughes, R. P.; Rheingold, A. L.; Herrmann, W. A.; Hubbard, J. L. *J. Organomet. Chem.* **1985**, *286*, 361.

(2) (a) Heidelberg. (b) Notre Dame. (c) München.

(3) Current address: Division of Chemistry, California Institute of Technology, Pasadena, CA 91125.

(4) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 6, Chapter 40.

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