syringe, with results given in the text.

1-Octen-4-one (14). ^{1}H NMR (CDCl$_3$), δ: 6.20–5.80 (m, 1 H), 5.178 (dd, J = 9.3, 1.2 Hz) and 5.134 (dd, J = 16.8, 1.2 Hz) (2 H), 3.167 (d, J = 6.6 Hz, 2 H), 2.440 (t, J = 7.5 Hz, 2 H), 1.561 (quintet, J = 7.5 Hz, 2 H), 1.325 (quintet, J = 7.5 Hz, 2 H), 0.904 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (CDCl$_3$), δ: 211.628, 130.744, 118.615, 47.730, 42.089, 25.828, 22.322, 13.821. IR (CDCl$_3$), cm^{-1}: 3160 nw), 3080 (w), 2960 (s), 2940 (s), 2880 (s), 1710 (s), 1635 (m), 1460 (m), 1380 (m). Retention time: GC, 7.8 min.

2-Octen-4-one. ^{1}H NMR (CDCl$_3$), δ: 6.95–6.75 (m, 1 H), 6.123 (dq, J = 15.9, 1.5 Hz, 1 H), 2.518 (t, J = 7.5 Hz, 2 H), 1.890 (dd, J = 6.6, 1.5 Hz, 3 H), 1.70–1.45 (m, 2 H), 1.321 (quintet, J = 7.2 Hz, 2 H), 0.913 (t, J = 7.2 Hz, 3 H). IR (CDCl$_3$), cm^{-1}: 3150 (w), 2950 (s), 2920 (s), 2860 (m), 1680 (s), 1660 (s), 1620 (s), 1450 (s), 1370 (s). Retention time: GC, 8.7 min.

Methyl Iodide Reaction. These reactions were performed as in the general procedure. Samples for monitoring by GC and IR and NMR spectroscopy were removed via syringe.

5-Hydroxy-5-methyl-6-decanone (15). ^{1}H NMR (CDCl$_3$), δ: 3.95–3.85 (broad, 1 H), 2.500 (dt, J = 11.1, 7.2 Hz, 2 H), 1.72–1.55 (m, 4 H), 1.40–1.20 (m, 6 H), 1.345 (s, 3 H), 0.926 (t, J = 7.5 Hz, 3 H), 0.881 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (CDCl$_3$), δ: 214.630, 78.708, 39.350, 35.433, 25.757, 25.548, 22.927, 22.398, 13.887. IR (CDCl$_3$), cm^{-1}: 3600–3400 (br, m), 2960 (s), 2940 (s), 2880 (s), 2870 (s), 1705 (s). MS, *m*/*e*: 187 (0.1%), 186 (0.2%), 102 (6.8%), 101 (100%), 83 (13.8%), 59 (9.1%), 57 (13.9%), 55 (18.6%), 45 (29.8%), 43 (26.3%), 41 (18.7%). Retention times: GC, 12.2 min; HPLC, 21 min.

Benzyl Bromide Reactions. These reactions were performed as in the General Procedure with the yields and times as indicated in the text. Samples for monitoring by GC and IR spectroscopy were removed via syringe.

1-Phenyl-2-hexanone (16). ^{1}H NMR (CD$_2$Cl$_2$), δ: 7.35–7.10 (m, 5 H), 3.660 (s, 2 H), 2.436 (t, J = 7.4 Hz, 2 H), 1.501 (quintet, J = 7.4 Hz, 2 H), 1.251 (sextet, J = 7.4 Hz, 2 H), 0.853 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (THF), δ: 207.115, 136.442, 130.578, 129.458, 127.643, 50.695, 42.318, 23.358, 14.617. IR (CDCl$_3$), cm^{-1}: 3100 (w), 3070 (w), 3040 (w), 2960 (m), 2940 (m), 2900 (w), 2880 (w), 1710 (s). MS, *m*/*e*: 176 (21.6%), 92 (12.4%), 91 (76.1%), 89 (14.4%), 85 (100%), 65 (32.6%), 63 (11.5%), 57 (77.3%), 44 (13.2%). Retention times: GC 13.0, min; HPLC, 17 min.

Bibenzyl (17). ^{1}H NMR (CDCl$_3$), δ: 7.35–7.10 (m, 10 H), 2.924 (s, 4 H). ^{13}C NMR (THF), δ: 143.009, 129.436, 129.297, 126.938, 39.209. MS, *m*/*e*: 182 (25.8%), 91 (100%), 65 (17.3%), 44 (12.6%). Retention times: GC, 14.5 min; HPLC, 9 min.

1,3-Diphenylacetone (18). ^{1}H NMR (CDCl$_3$), δ: 7.40–7.10 (m, 10 H), 3.719 (s, 4 H). IR (CDCl$_3$), cm^{-1}: 3090, 3070, 3030, 1710. MS, *m*/*e*: 210 (20.8%), 118 (10.0%), 91 (100%), 65 (20.1%), 44 (20.0%). Retention times: GC, 17.4 min; HPLC, 10 min.

5-Benzyl-5-hydroxy-6-decanone (19). ^{1}H NMR (CDCl$_3$), δ: 7.30–7.15 (m, 5 H), 3.698 (s, 1 H), 2.980 (dd, J = 17.1, 14.1 Hz, 2 H), 2.488 (ddd, J = 22.2, 8.7, 6.3 Hz, 1 H), 1.92–1.20 (m, 11 H), 0.895 (t, J = 7.2 Hz, 3 H), 0.878 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (THF), δ: 214.921, 138.133, 131.561, 130.752, 129.539, 128.831, 127.415, 83.078, 49.760, 46.502, 40.322, 38.591, 26.458, 24.335, 23.444, 14.736. IR (CDCl$_3$), cm^{-1}: 3600–3400 (w), 3090 (w), 3070 (w), 3030 (w), 2960 (s), 2940 (s), 2880 (m), 1710 (s). MS, *m*/*e*: 262 (0.3%), 177 (100%), 91 (29.2%), 85 (17.7%), 57 (17.7%). Retention times: GC, 18.6 min; HPLC, 27 min.

1,2-Diphenyl-3-heptanone (20). ^{1}H NMR (CDCl$_3$), δ: 7.32–7.00 (m, 10 H), 3.919 (t, J = 7.5 Hz, 1 H), 3.420 (dd, J = 13.8, 7.8 Hz, 1 H), 2.895 (dd, J = 13.5, 6.9 Hz, 1 H), 2.295 (dd, J = 17.7, 7.5 Hz, 1 H), 2.271 (dd, J = 17.1, 7.5 Hz, 1 H), 1.44–1.30 (m, 2 H), 1.101 (sextet, J = 7.2 Hz, 2 H), 0.751 (t, J = 7.2 Hz, 3 H). ^{13}C (CD$_2$Cl$_2$), δ: 210.486, 140.858, 139.693, 129.857, 129.640, 129.339, 129.080, 128.110, 126.945, 43.264, 42.887, 39.392, 26.903, 26.593, 23.279, 22.958, 14.573, 14.414. IR (CDCl$_3$), cm^{-1}: 3090 (w), 3070 (w), 3030 (w), 2960 (s), 2940 (m), 2880 (w), 1710 (s). MS, *m*/*e*: 266 (74.0%), 209 (25.1%), 181 (71.6%), 85 (100%), 57 (46.6%). Retention times: GC, 20.0 min; HPLC, 29 min.

5-Hydroxy-5-allyl-6-decanone (27a). ^{1}H NMR (CDCl$_3$), δ: 5.62–5.76 (m, 1 H), 5.078 (d, J = 16.5 Hz) and 5.068 (d, J = 10.8 Hz) (2 H), 3.80–4.00 (broad, 1 H), 2.38–2.52 (m, 4 H), 1.702 (dd, J = 8.7, 7.8 Hz) and 1.577 (quintet, J = 7.5 Hz) (4 H), 1.30–1.50 (m, 6 H), 0.896 (dt, J = 12.6, 7.2 Hz, 6 H). ^{13}C NMR (CDCl$_3$), δ: 213.758, 132,482, 118.376, 81.361, 43.506, 38.329, 36.129, 35.819, 25.452, 22.952, 22.418, 13.886. IR (CDCl$_3$), cm^{-1}: 3400–3600 (br, m), 2950 (s), 2930 (s), 2860 (s), 1700 (s), 1635 (m). MS, *m*/*e*: 213 (0.2%), 171 (10.0%), 127 (18.1%), 86 (5.7%), 85 (100%), 57 (32.2%), 55 (4.8%), 43 (4.7%), 41 (13.5%).

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Preparation and Spectral Properties of a Series of Bis(phosphite) Alkyne Complexes and X-ray Crystal Structure of [WI$_2$(CO){P(OMe)$_3$}$_2$(η^2-MeC$_2$Me)]

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The complexes [WI$_2$(CO)(NCMe)(η^2-RC$_2$R)$_2$] (R = Me, Ph) react with 2 equiv of P(OR′)$_3$ (R′ = Me, Et, ^{i}Pr, ^{n}Bu) in CH$_2$Cl$_2$ at room temperature to give the four-electron alkyne compounds [WI$_2$(CO){P(OR′)$_3$}$_2$(η^2-RC$_2$R)] (**1**–**8**) via displacement of acetonitrile and an alkyne ligand, respectively. X-ray single-crystal crystallographic studies were carried out on the complex [WI$_2$(CO){P(OMe)$_3$}$_2$(η^2-MeC$_2$Me)] (**1**). Crystals of **1** are orthorhombic, space group *Pnab*, in a unit cell of dimensions a = 14.214 (12), b = 15.332 (12), and c = 20.350 (25) Å. The structure was refined to R = 0.062 for 2164 reflections with $I > 3\sigma(I)$. The coordination geometry around tungsten in **1** may be considered in terms of a pseudooctahedral structure. The complex has cis-iodide ligands, which are trans to a P(OMe)$_3$ and a but-2-yne ligand. The other two sites are occupied by carbonyl and P(OMe)$_3$ ligands. ^{31}P NMR studies are interpreted in order to suggest the geometry of complexes **1**–**8** in solution. The barrier to but-2-yne rotation of **1** is 55.3 kJ mol^{-1}. ^{13}C NMR chemical shifts of the alkyne contact carbons above 200 ppm in these complexes indicate that the alkyne ligand is acting as a four-electron donor in these compounds.

Introduction

Alkyne complexes of molybdenum and tungsten have become increasingly important in recent years, mainly due to their ability to act as two- and four-electron donors in a variety of complexes.[1] Molybdenum(II) and tungsten(II) alkyne complexes containing cyclopentadienyl or indenyl[2] and dithiocarbamates[3] as attached

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(1) Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.* **1982**, *21*, 466. Templeton, J. L.; Winston, P. B.; Ward, B. C. *J. Am. Chem. Soc.* **1981**, *103*, 7713.

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Table I. Physical and Analytical[a] Data for the $[WI_2(CO)\{P(OR')_3\}_2(\eta^2\text{-}RC_2R)]$ Complexes

complex	color	% yield of pure product	% C	% H
$[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$ (**1**)	purple	82	17.5 (17.2)	3.3 (3.2)
$[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}PhC_2Ph)]$ (**2**)	dk green	43	28.6 (28.3)	3.2 (3.2)
$[WI_2(CO)\{P(OEt)_3\}_2(\eta^2\text{-}MeC_2Me)]$ (**3**)	dk green	75	24.2 (24.0)	4.3 (4.3)
$[WI_2(CO)\{P(OEt)_3\}_2(\eta^2\text{-}PhC_2Ph)]$ (**4**)	dk green	48	33.8 (33.2)	4.1 (4.1)
$[WI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}MeC_2Me)]$ (**5**)	dk green	68	29.2 (29.5)	5.1 (5.2)
$[WI_2(CO)\{P(O^iPr)_3\}_2(\eta^2\text{-}PhC_2Ph)]$ (**6**)	dk green	40	37.8 (37.4)	4.9 (4.9)
$[WI_2(CO)\{P(O^nBu)_3\}_2(\eta^2\text{-}MeC_2Me)]$ (**7**)	dk green	69	34.7 (34.1)	6.0 (5.9)
$[WI_2(CO)\{P(O^nBu)_3\}_2(\eta^2\text{-}PhC_2Ph)]$ (**8**)	dk green	45	41.2 (40.9)	5.8 (5.6)

[a] Calculated values in parentheses.

Table II. IR Data[a] for the $[WI_2(CO)\{P(OR')_3\}_2(\eta^2\text{-}RC_2R)]$ Complexes

complex	ν(CO)/ cm^{-1}	ν(C≡C)/ cm^{-1}	complex	ν(CO)/ cm^{-1}	ν(C≡C)/ cm^{-1}
1	1985 (s)	1630 (vw)	**5**	1955 (s)	1658 (vw)
2	1990 (s)	1638 (vw)	**6**	1963 (s)	1682 (vw)
3	1978 (s)	1660 (w)	**7**	1975 (s)	1656 (vw)
4	1980 (s)	1680 (vw)	**8**	1980 (s)	1680 (vw)

[a] All spectra were recorded in $CHCl_3$ as thin films between NaCl plates. Abbreviations: s, strong; w, weak; vw, very weak.

ligands have received considerable attention in the past. However, only more recently have halide alkyne complexes of molybdenum(II) and tungsten(II) been investigated.[4] Apart from our work the only iodo complexes of this type to be reported are $[MoI(CNR)_4(\eta^2\text{-}{}^tBuNHC_2NH^tBu)]I$ (R = Me, ^{t}Bu) and related complexes by Lippard and co-workers[5] and $[WI_2(CO)_2L(\eta^2\text{-}PhC_2H)]$ (L = PMe_3, $AsMe_3$, CN^tBu) by Umland and Vahrenkamp.[6]

In recent years we have been investigating the chemistry of the highly versatile complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph),[7] which are prepared in good yield from reaction of $[WI_2(CO)_3(NCMe)_2]$[8] with 2 equiv of RC_2R in CH_2Cl_2. In this paper we wish to describe the reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with phosphites. Preliminary results of this work have been described in an earlier communication.[9]

Experimental Section

The complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph) were synthesized by the literature method.[7] All preparations were carried out on a vacuum Schlenk line. Isolated products were stored in Schlenk tubes. Dichloromethane was dried by refluxing over P_2O_5. All chemicals were purchased from commercial sources.

Elemental analyses (C, H, and N) were recorded on a Carlo Erba MOD 1106 elemental analyzer (using helium as the carrier gas). Infrared spectra were recorded on a Perkin-Elmer 197 infrared spectrophotometer. (All spectra were recorded in $CHCl_3$ as thin films between NaCl plates.) ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on either a JEOL FX 60 NMR spectrometer, a Bruker WH-400 NMR spectrometer (University of Warwick), or a Bruker WP 80 NMR spectrometer (University of Manchester). ^{1}H and ^{13}C NMR spectra were referenced to tetramethylsilane. ^{31}P NMR spectra were referenced to H_3PO_4.

Syntheses. $[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$ (1). To $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ (0.320 g, 0.520 mmol) dissolved in dichloromethane (10 cm^3) was added $P(OMe)_3$ (0.12 cm^3, 0.129 g, 1.04 mmol). After 17 h, filtration and removal of solvent in vacuo gave a purple-green solid. Purple crystals of **1** were isolated from a dichloromethane/diethyl ether mixture at −18 °C. Yield: 0.33 g, 82%. Compounds **3**, **5**, and **7** were prepared in a similar manner. For colors and yields, see Table I.

$[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}PhC_2Ph)]$ (2). To $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ (0.440 g, 0.510 mmol) dissolved in dichloromethane (15 cm^3) was added $P(OMe)_3$ (0.14 cm^3, 0.13 g, 1.07 mmol). After 17 h, filtration and solvent removal in vacuo gave a deep green oil, which was purified by column chromatography on a silica column (column developed with diethyl ether and the compound eluted with dichloromethane). Solvent removal in vacuo gave a green crystalline powder of **2**. Yield: 0.20 g, 43%. Compounds **4**, **6**, and **8** were prepared in a similar manner. For colors and yields, see Table I.

Crystal Data. Crystals were prepared as described above. Standard reflections were measured during the course of the data collection, but no deterioration was observed. Crystallographic data for the complex $[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$ (**1**) are given in Table V.

A crystal of approximate size 0.25 × 0.3 × 0.3 mm was set up to rotate about the *a* axis on a Stoe Stadi2 diffractometer fitted with a monochromator, and data were collected via variable-width ω scan. Background counts were for 20 s, and a scan rate of 0.0333°/s was applied to a width of $(1.5 + \sin \mu/\tan \theta)°$. A total of 3588 independent reflections, with ($2\theta < 50°$) $0 \leq h < 16$, $0 \leq k < 18$, and $0 \leq l < 24$, were measured, of which 2164 with $I > 3\sigma(I)$ were used in subsequent refinement. An empirical absorption correction was applied.[10] (Max-

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(2) Davidson, J. L.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* **1975**, 2531. Howard, J. A. K.; Stanfield, R. F. D. *J. Chem. Soc., Dalton Trans.* **1976**, 246. Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1976**, 738. Bottrill, M.; Green, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2365. Faller, J. W.; Murray, H. H. *J. Organomet. Chem.* **1979**, *172*, 171. Sünkel, K.; Nagel, U.; Beck, W. *J. Organomet. Chem.* **1981**, *222*, 251. Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 2698.

(3) McDonald, J. W.; Newton, W. E.; Creedy, C. T. C.; Corbin, J. L. *J. Organomet. Chem.* **1975**, *92*, C25. Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J.-J.; McDonald, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1318. Herrick, R. S.; Templeton, J. L. *Organometallics* **1982**, *1*, 842. Templeton, J. L.; Herrick, R. S.; Morrow, J. R. *Organometallics* **1984**, *3*, 535.

(4) (a) Davidson, J. L.; Vasapollo, G.; Manojlovic-Muir, M.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1982**, 1025. (b) Winston, P. B.; Burgmayer, S. J. N.; Templeton, J. L. *Organometallics* **1983**, *2*, 167. (c) Davidson, J. L.; Vasapollo, G. *Polyhedron* **1983**, *2*, 305. (d) Davidson, J. L.; Vasapollo, G. *J. Chem. Soc., Dalton Trans.* **1985**, 2239. (e) Bennett, M. A.; Boyd, I. W. *J. Organomet. Chem.* **1985**, *290*, 165. (f) Winston, P. B.; Burgmayer, S. J. N.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1986**, *5*, 1707. (g) Mayr, A.; Lee, K. S.; Kjelsberg, M. A.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 6079.

(5) Lam, C. T.; Corfield, P. W. R.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 617. Giandomenico, C. M.; Lam, C. T.; Lippard, S. J. *J. Am. Chem. Soc.* **1982**, *104*, 1263. Caravana, C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1982**, *21*, 1860. Hoffmann, R.; Wilker, C. N.; Lippard, S. J.; Templeton, J. L.; Brower, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 146. Bianconi, P. A.; Williams, I. D.; Engeler, M. P.; Lippard, S. J. *J. Am. Chem. Soc.* **1986**, *108*, 311. Warner, S.; Lippard, S. J. *Organometallics* **1986**, *5*, 1716.

(6) Umland, P.; Vahrenkamp, H. *Chem. Ber.* **1982**, *115*, 3580.

(7) Armstrong, E. M.; Baker, P. K.; Drew, M. G. B. *Organometallics* **1988**, *7*, 319.

(8) Baker, P. K.; Fraser, S. G.; Keys, E. M. *J. Organomet. Chem.* **1986**, *309*, 319.

(9) Baker, P. K.; Keys, E. M. *Inorg. Chim. Acta* **1986**, *116*, L49.

(10) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

Table III. ^{1}H NMR Data[a] for the $[WI_2(CO)\{P(OR')_3\}_2(\eta^2\text{-}RC_2R)]$ Complexes

complex	$\delta(^1H)$/ppm
1	2.93 (6 H, s, MeC_2)
	3.49 (9 H, d, J_{PH} = 10.8 Hz, O*Me*)
	4.00 (9 H, d, J_{PH} = 10.2 Hz, O*Me*)
2	3.60 (18 H, t, J_{PH} = 10.9 Hz, *Me*)
	7.40 (10 H, m, *Ph*)
3	1.32 (18 H, q, J = 5.4 Hz, CH_2CH_3)
	2.93 (3 H, t, J_{PH} = 1.0 Hz, MeC_2)
	3.10 (3 H, t, J_{PH} = 1.8 Hz, MeC_2)
	3.42 (12 H, m, CH_2CH_3)
4	1.15 (18 H, m, CH_2CH_3)
	4.00 (12 H, m, CH_2CH_3)
	7.39 (10 H, m, Ph)
5	1.20 (36 H, d, J_{PH} = 6.35 Hz, *Me*)
	3.09 (6 H, s, MeC_2)
	4.73 (6 H, m, C–*H*)
6	1.06 (36 H, m, J_{HH} = 6.6 Hz, *Me*)
	4.78 (6 H, m, C–*H*)
	7.48 (10 H, m, *Ph*)
7	0.90 (18 H, m, *Me*)
	1.47 (24 H, m, $CH_2CH_2CH_3$)
	2.92 (3 H, t, J_{PH} = 0.5 Hz, MeC_2)
	3.09 (3 H, t, J_{PH} = 0.6 Hz, MeC_2)
	3.90 (6 H, m, OCH_2)
	4.24 (6 H, m, OCH_2)
8	0.87 (18 H, m, *Me*)
	1.38 (24 H, m, $CH_2CH_2CH_3$)
	3.90 (12 H, m, OCH_2)
	7.48 (10 H, m, *Ph*)

[a] Spectra were recorded in $CDCl_3$ (25 °C) and referenced to $SiMe_4$. Abbreviations: d, doublet; m, multiplet; q, quartet; s, singlet; t, triplet.

Table IV. ^{13}C NMR Data[a] for the $[WI_2(CO)\{P(OR')_3\}_2(\eta^2\text{-}RC_2R)]$ Complexes

complex	$\delta(^{13}C)$/ppm
1	232.21 (s, $C{\equiv}C$), 206.10 (s, *C*O), 54.19 (s, O*Me*), 22.69 (s, MeC_2)
2	220.52 (s, $C{\equiv}C$), 208.08 (s, *C*O), 139.3 (s, *Ph-i*-C), 130.21 (s, *Ph o-C*), 128.39 (*Ph m*-C), 126.96 (s, *Ph p-C*), 54.06 (s, O*Me*)
3	223.64 (s, $C{\equiv}C$), 210.44 (s, *C*O), 62.76, 62.5, 62.24 (s, CH_2), 24.04, 21.7 (s, MeC_2), 15.98 (s, *Me*)
4	220.59 (s, $C{\equiv}C$), 202.01 (s, *C*O), 139.38, 138.0 (s, *Ph-i*-C), 131.51 (s, *Ph o-C*), 129.95 (s, *Ph m*-C), 128.26 (s, *Ph p-C*), 63.8, 65.02, 62.76, 62.5, 62.1, 61.73 (b, m CH_2), 16.11 (s, *Me*)
5	217.79 (s, $C{\equiv}C$), 201.28 (s, *C*O), 70.82 (s, *C*H), 31.19 (s, *Me*), 23.91 (s, MeC_2)
6	220.51 (t, $C{\equiv}C$), 218.17 (t, $C{\equiv}C$), 203.36 (s, *C*O), 139.55 (s, *Ph-i*-C), 129.80 (s, *Ph o-C*), 129.15 (s, *Ph m-C*), 127.15 (s, Ph *p-C*), 71.34 (s, *C*H), 44.69 (s, *Me*)
7	223.38 (t, $C{\equiv}C$), 200.42 (s, *C*O), 66.27 (s, OCH_2), 32.49 (s, CH_2), 22.32 (s, MeC_2), 18.84 (s, CH_2), 13.77 (s, *Me*)
8	221.17, 217.52 (s, $C{\equiv}C$), 207.78 (s, CO), 139.69 (s, *Ph-i*-C), 129.95 (s, *Ph o-C*), 128.91 (s, *Ph m-C*), 128.13 (s, *Ph p-C*), 66.53 (s, OCH_2), 32.23 (s, CH_2), 18.84 (s, CH_2), 13.77 (s, *Me*)

[a] Spectra recorded in $CDCl_3$ (+25 °C) referenced to Me_4Si. Abbreviations: b, broad; m, multiplet; s, singlet; t, triplet.

imum and minimum transmission factors were 0.80 and 0.25, respectively.) The structure was determined by the heavy-atom method. All non-hydrogen atoms were refined anisotropically. The methyl hydrogen atoms were refined as rigid groups with a common refined thermal parameter.

Weights used in the least-squares refinement were of the form $w = 1/[\sigma^2(F) + 0.003F^2]$. The final R values were 0.062 (R_w = 0.067). In the final cycle of refinement all shift/error ratios were $<0.3\sigma$. The final difference Fourier map showed no peaks greater than 1.5 e Å^{-3}. Calculations were carried out by using SHELX 76[11] and some of our own programs on the Amdahl V7 computer at the University of Reading.

Table V. Crystallographic Data for $[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$ (**1**)

chem formula $WI_2P_2O_7C_{11}H_{24}$
a = 14.214 (12)[a] Å
b = 15.332 (12)[a] Å
c = 20.350 (25)[a] Å
V = 4435 Å^3
Z = 8
T = 298 °C
λ = 0.7107 Å

fw = 767.9
space group *Pnab* (No. 60)
ρ_{obsd} = 2.30 g cm^{-3}; ρ_{calcd} = 2.28 g cm^{-3}
μ = 38.26 cm^{-1}
transmission coeff: max 0.80; min 0.25
$R(F_o)$ = 0.062
$R_w(F_o)$ = 0.067

[a] Esd's are in parentheses.

Table VI. Atomic Coordinates (×10^4) with Estimated Standard Deviations in Parentheses for $[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$ (**1**)

atom	*x*	*y*	*z*
W(1)	163 (1)	2448.4 (4)	1493.6 (4)
I(1)	1558 (1)	1162 (1)	1360 (1)
I(2)	1490 (1)	3704 (1)	1071 (1)
P(1)	−243 (4)	2198 (4)	312 (3)
P(2)	−782 (4)	3786 (4)	1502 (3)
O(11)	−1203 (10)	2588 (11)	108 (8)
O(12)	397 (11)	2569 (12)	−247 (8)
O(13)	−324 (11)	1191 (9)	166 (8)
C(11)	−1400 (14)	3116 (16)	−450 (10)
C(12)	1319 (17)	2204 (22)	−390 (14)
C(13)	−685 (21)	832 (18)	−403 (13)
O(21)	−1819 (10)	3538 (10)	1724 (9)
O(22)	−516 (12)	4598 (10)	1956 (8)
O(23)	−936 (11)	4270 (9)	835 (8)
C(21)	−2545 (16)	4209 (16)	1801 (13)
C(22)	−364 (29)	4483 (17)	2616 (13)
C(23)	−881 (25)	5169 (15)	703 (14)
C(100)	733 (17)	2697 (17)	2359 (12)
O(100)	1023 (15)	2769 (14)	2868 (10)
C(51)	−1077 (18)	1818 (17)	2834 (14)
C(52)	−723 (16)	1939 (11)	2178 (13)
C(53)	−1064 (16)	1767 (14)	1570 (13)
C(54)	−1846 (16)	1341 (19)	1290 (18)

Table VII. Molecular Dimensions in the Coordination Sphere for $[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$ (**1**)

	Distances (Å)		
W(1)–I(1)	2.809 (2)	W(1)–C(100)	1.975 (25)
W(1)–I(2)	2.829 (2)	W(1)–C(52)	2.034 (19)
W(1)–P(1)	2.502 (6)	W(1)–C(53)	2.039 (23)
W(1)–P(2)	2.451 (6)		
	Angles (deg)		
I(1)–W(1)–I(2)	88.75 (6)	I(2)–W(1)–C(52)	152.0 (7)
I(1)–W(1)–P(1)	87.85 (13)	P(1)–W(1)–C(52)	117.1 (8)
I(2)–W(1)–P(1)	88.05 (14)	P(2)–W(1)–C(52)	88.7 (5)
I(1)–W(1)–P(2)	167.05 (15)	C(100)–W(1)–C(52)	73.6 (11)
I(2)–W(1)–P(2)	78.35 (15)	I(1)–W(1)–C(53)	104.6 (6)
P(1)–W(1)–P(2)	90.48 (19)	I(2)–W(1)–C(53)	160.4 (6)
I(1)–W(1)–C(100)	86.1 (6)	P(1)–W(1)–C(53)	78.3 (7)
I(2)–W(1)–C(100)	82.3 (8)	P(2)–W(1)–C(53)	87.7 (6)
P(1)–W(1)–C(100)	168.7 (7)	C(100)–W(1)–C(53)	112.4 (10)
P(2)–W(1)–C(100)	93.3 (6)	C(52)–W(1)–C(53)	38.8 (9)
I(1)–W(1)C(52)	103.5 (5)		

Positional parameters are given in Table VI, and molecular dimensions in the coordination sphere, in Table VII.

Results

Reaction of the complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me, Ph) with 2 equiv of $P(OR')_3$ (R′ = Me, Et, ^{i}Pr, ^{n}Bu) in CH_2Cl_2 at room temperature gave the highly colored bis(phosphite) alkyne complexes $[WI_2(CO)\{P(OR')_3\}_2(\eta^2\text{-}RC_2R)]$ (**1**–**8**) in good yield. The complexes **1**–**8** have been fully characterized by elemental analysis (C, H, and N) (Table I), IR spectroscopy (Table II), and ^{1}H and ^{13}C NMR spectroscopy (Tables III and IV). The complexes are all moderately air-sensitive (particularly in solution) and are best stored under nitrogen in Schlenk tubes. The but-2-yne complexes are soluble in hydrocarbon solvents, whereas the diphenylacetylene compounds are less soluble, although they are very soluble in $CHCl_3$ and CH_2Cl_2.

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[11] Sheldrick, G. M. "Shelx 76 Package for Crystal Structure Determination", University of Cambridge, 1976.

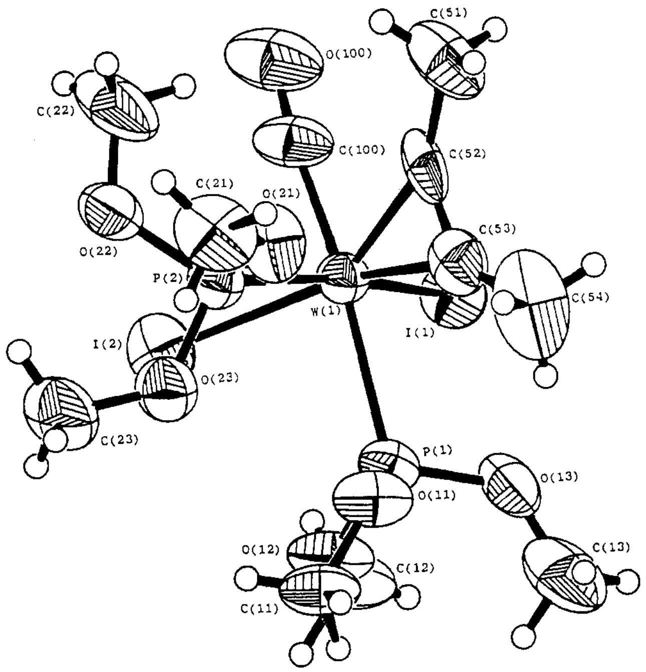

Figure 1. Structure of $[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$ (**1**) with thermal ellipsoids at 50% probability.

Discussion

Description of the Molecular Structure of $[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$ (1). The structure consists of discrete units of $[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$, and the molecule is shown in Figure 1 together with the atomic numbering scheme. The tungsten atom is bonded to two iodine atoms, two trimethyl phosphite groups through phosphorus, a carbonyl group, and an alkyne. The geometry around the tungsten atom is best considered as distorted octahedral, considering the alkyne to occupy one site in the coordination sphere trans to the iodine atom I(2). As is common in d^4 systems,[4f] the alkyne is parallel to the M–CO axis, a configuration that optimizes both the π-donor and π-acceptor roles of the alkyne ligand. The W–P(2) bond [trans to I(1)] is significantly shorter at 2.451 (6) Å than W–P (1) at 2.502 (6) Å, which is trans to the carbonyl group. Remaining bond lengths are unremarkable [W–I(1) = 2.809 (2), W–I(2) = 2.829 (2), W–C(100) = 1.975 (25), W–C(52) = 2.034 (19), W–C(53) = 2.039 (23) Å].

Least-squares planes calculations show that the equatorial plane (consisting of atoms W(1), I(1), I(2), P(2), and the alkyne group) is slightly nonplanar. Thus, for the plane through I(1), I(2), P(2), and the midpoint of the alkyne group C(5m), the deviations of the contributing atoms are −0.05, 0.06, −0.07, and 0.07 Å, respectively. The alkyne group is approximately perpendicular to this equatorial plane and intersects it at an angle of 88.8 (1)°.

The alkyne retains multiple-bond character with a central bond length of 1.354 (32) Å. The C–C–C angles are 133 (3) and 141 (3)°; however, it is doubtful whether the difference is significant.

The remaining dimensions are as expected. There are no intermolecular distances less than the sum of van der Waals radii between the ions.

There are very few structures comparable to **1**, but one example of a group VI alkyne complex of similar formulation is *cis*-$[MoBr_2(CO)(PEt_3)_2(\eta^2\text{-}PhC_2H)]$.[4f] The structure of the *cis*-[Mo(CO)(alkyne)] moiety is equivalent to that in **1**, but the arrangement of the remaining atoms is very different; thus, the phosphines are mutually trans by comparison with **1**, where the phosphites are mutually cis, and in addition have a halide trans to carbonyl, while **1** has phosphite trans to carbonyl. Variations in bond lengths between the two structures are as expected, given the differences in atom type.

Reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with Phosphite Donor Ligands. The reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with $P(OR')_3$ probably involves initial displacement of the acetonitrile ligand via an associative mechanism to give $[WI_2(CO)\{P(OR')_3\}(\eta^2\text{-}RC_2R)_2]$, which reacts with a second 1 equiv of $P(OR')_3$ to afford the observed products $[WI_2(CO)\{P(OR')_3\}_2(\eta^2\text{-}RC_2R)]$ (**1–8**). One of the alkyne ligands in $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ can alter its mode of bonding from a four-electron donor to a two-electron donor to give the seven-coordinate intermediates $[WI_2(CO)(NCMe)\{P(OR')_3\}(\eta^2\text{-}RC_2R)_2]$, which rapidly lose acetonitrile to allow the alkyne to revert back to being a four-electron donor. Associative mechanisms have been proposed for reactions of donor ligands with alkyne complexes of molybdenum(II) and tungsten(II) containing cyclopentadienyl and indenyl[12] or dithiocarbamate[13] ligands. Reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with 1 equiv of $P(OMe)_3$ in CH_2Cl_2 afforded a 1:1 mixture of $[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$ and $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$. However, reaction of the larger and poor electron-donating phosphite ligand $P(OPh)_3$ in refluxing $CHCl_3$ for 48 h gave a mixture of the mono(phosphite) product $[WI_2(CO)\{P(OPh)_3\}(\eta^2\text{-}MeC_2Me)_2]$ [ν(CO) = 2020 cm^{-1}], the bis(phosphite) complex $[WI_2(CO)\{P(OPh)_3\}_2(\eta^2\text{-}MeC_2Me)]$ [ν(CO) = 1980 cm^{-1}], and unreacted starting material [ν(CO) = 2050 cm^{-1}]. Similarly, equimolar quantities of $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ and $P(OPh)_3$ in refluxing $CHCl_3$ (48 h) give $[WI_2(CO)\{P(OPh)_3\}(\eta^2\text{-}PhC_2Ph)_2]$ [ν(CO) = 2030 cm^{-1}]. $[WI_2(CO)\{P(OPh)_3\}_2(\eta^2\text{-}PhC_2Ph)]$ [ν(CO) = 1990 cm^{-1}], and $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ [ν(CO) = 2090 cm^{-1}]. There was extensive decomposition in these reactions, and it was not possible to separate and isolate the mono- and bis(triphenyl phosphite) complexes from these reactions. It is likely that reactions of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with 1 equiv of $P(OR')_3$ go with retention of configuration since reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeC_2Me)_2]$ with carbon monoxide gives the *trans*-dicarbonyl compound $[WI_2(CO)_2(\eta^2\text{-}MeC_2Me)_2]$. The structure of $[WI_2(CO)_2(\eta^2\text{-}MeC_2Me)_2]$ was determined by X-ray crystallography.[14] The carbonyl stretching bands for the mono(phosphite) compounds $[WI_2(CO)\{P(OPh)_3\}(\eta^2\text{-}RC_2R)_2]$ are at lower wavenumber compared to that of the mono(acetonitrile) precursors, which was not expected since phosphites are much stronger π-acceptors compared to acetonitrile. It is probable that a trigonal twist occurs to give complex c of Scheme I with an iodide trans to carbon monoxide, which can react with a second 1 equiv of phosphite ligand to give the trans-phosphite compound shown in Scheme Id. Templeton and co-workers[4b,f] have previously reported the X-ray crystal structure of $[MoBr_2(CO)(PEt_3)_2(\eta^2\text{-}PhC_2H)]$, which has the geometry shown in Scheme Id. Also Davidson and Vasapollo[4d] observed trans-phosphine geometry for their complexes $[WBr_2(CO)(PPh_3)_2(\eta^2\text{-}RC_2R')]$ (R = R' = Me, Ph; R = Me, R' = Ph).

The room-temperature ^{31}P NMR spectrum of **1** ($CDCl_3$) showed resonances due to the cis isomer (Figure 1) at δ = 112.12 (d, J_{PP} = 29.7 Hz, J_{WP} = 286.7 Hz) and δ = 105.31 (d, J_{PP} = 29.8 Hz, J_{WP} = 484.6 Hz) and also a weak resonance at δ = 106.95 (s, J_{WP} = 413.7 Hz), which is likely to be due to the trans isomer (Scheme Id). It is interesting to note that the color of the solution after growing purple crystals of the cis isomer (Figure 1) is decidedly green, i.e. the same as complexes **2–8** and also of $[WBr_2(CO)(PEt_3)_2(\eta^2\text{-}PhC_2H)]$, which was shown to have the trans structure[4f] shown in Scheme Id. The less soluble cis isomer crystallizes out leaving the more soluble trans isomer of **1** in solution. It is interesting to note that the ^{31}P NMR spectrum of **1** before crystallization indicates a 2:1 ratio of cis:trans isomers. After crystallization, the ^{31}P NMR spectrum of the mother liquor shows the cis and trans isomers to be present in equal amounts; hence, as expected, there has been an enrichment of the trans signal. After 2 days, the ^{31}P NMR spectrum of this liquor shows

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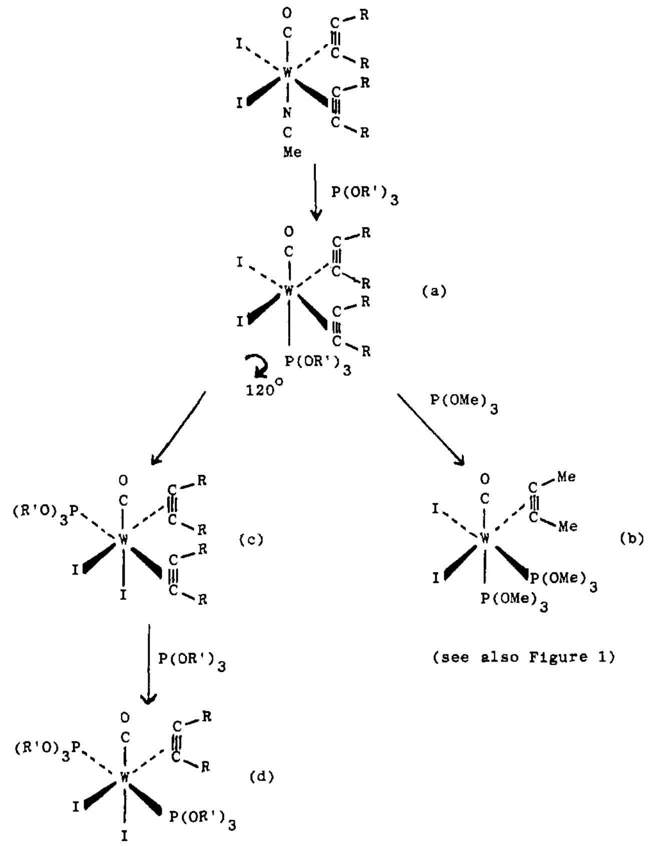
(12) Allen, S. R.; Baker, P. K.; Barnes, S. G.; Green, M.; Trollope, L.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1981**, 873.

(13) Herrick, R. S.; Leazer, D. M.; Templeton, J. L. *Organometallics* **1982**, *2*, 834.

(14) Armstrong, E. M.; Baker, P. K.; Drew, M. G. B. *J. Organomet. Chem.* **1987**, *336*, 377.

Scheme I. Proposed Mechanism for the Reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R)_2]$ with $P(OR')_3$



an equilibrium mixture, i.e. a ratio of 2:1 of cis:trans isomer in solution. This is accompanied by a color change from green to purple green. Trimethyl phosphite has a smaller cone angle[15] (θ = 107°) compared to those of other phosphite and phosphine ligands, and hence after formation of the mono(phosphite) complex (Scheme Ia), simple substitution of an alkyne ligand affords the crowded cis-trimethyl phosphite complex shown in Scheme Ib or Figure 1. The small amount of trans isomer of **1** is probably formed via the trigonal-twist mechanism shown in Scheme I. However, a trigonal twist can interconvert compound d to compound b of Scheme I and vice versa; hence, this mechanism cannot be ruled out. It is also possible that these rearrangements could occur by a ligand dissociation mechanism. The room-temperature ^{31}P NMR spectra of **5** and **6** ($CDCl_3$) showed only single resonances at δ = 4.80 (s, J_{WP} = 578.7 Hz) and 94.44 (s, J_{WP} = 414.3 Hz), respectively, which suggests the trans isomer shown in Scheme Id. Finally, it should be noted that Davidson and Vasapollo[4d] found cis–trans isomerism for their dibromo complex $[WBr_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$; however, from their detailed NMR studies they postulated a cis isomer different from that shown in Figure 1, i.e. with trans-bromide ligands and cis-trimethyl phosphite ligands.

Infrared Spectra. The infrared spectra of **1–8** as expected all show a single carbonyl band between 1955 and 1990 cm^{-1}. The more electron-rich but-2-yne complexes have slightly lower carbonyl stretching bands compared to those of their diphenylacetylene counterparts. The alkyne stretching bands for **1–8** are all lower than those of the uncoordinated alkyne ligands. This is to be expected since there is considerable back-donation of electron density from the metal to the empty π^*-orbitals of the alkyne ligands, as shown by the bending back of the but-2-yne methyl carbons illustrated in Figure 1.

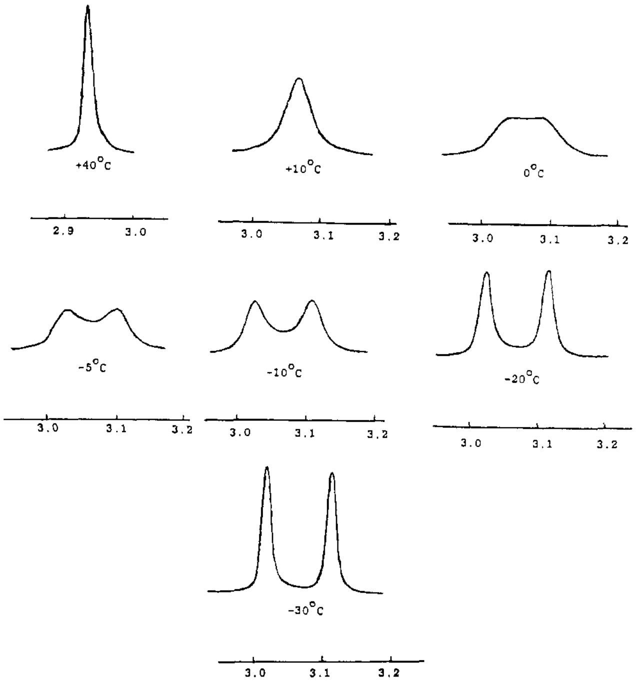


Figure 2. ^1H NMR spectra of the but-2-yne methyl protons of $[WI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC_2Me)]$ (**1**) from +40 to −30 °C.

^{1}H and ^{13}C NMR Studies. The ^1H NMR spectra of **1–8** showed the expected features for the structures shown in Figure 1 and Scheme Id. The barrier to but-2-yne rotation of **1** was determined by variable-temperature ^1H NMR spectroscopy. The activation barrier for **1** was calculated by using the Gutowsky–Holm equations[16] and was found to be 55.3 kJ mol^{-1} (T_c = 273 K, $\Delta\nu$ = 38.35 Hz). This value is in accord with those found by other workers[4d,f,12] for four-electron alkyne complexes of molybdenum(II) and tungsten(II). Variable-temperature spectra showing the but-2-yne methyl resonances are presented in Figure 2.

The ^{13}C NMR spectra of **1–8** all showed alkyne contact carbon resonance values above 200 ppm. These values indicated that the alkyne carbons are donating a total of four electrons to the metal in these complexes, since Templeton and Ward[17] have correlated alkyne contact carbon chemical shifts with the number of electrons donated to the metal. This mode of bonding with the alkyne ligand utilizing both sets of filled π-orbitals allows complexes **1–8** to obey the effective atomic number rule.

Acknowledgments. We wish to thank Dr. O. W. Howarth (University of Warwick) for measuring several ^1H, ^{13}C, and ^{31}P NMR spectra and J. Friend (University of Manchester) for recording several ^{31}P NMR spectra, and we thank the SERC for support.

Supplementary Material Available: For **1**, tables of remaining molecular dimensions not included in the paper, anisotropic and isotropic thermal parameters, and hydrogen atom coordinates (4 pages); a table of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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(15) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(16) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228. Allerhand, A.; Gutowsky, H. S.; Jones, J.; Meinzer, R. A. *J. Am. Chem. Soc.* **1966**, *88*, 3185.

(17) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.