

## Reaction of Molybdenum and Tungsten Alkylidyne Complexes with 2,6-Xylyl Isocyanide and Carbon Monoxide; Structural and Mechanistic Evidence for Novel Insertion Reactions

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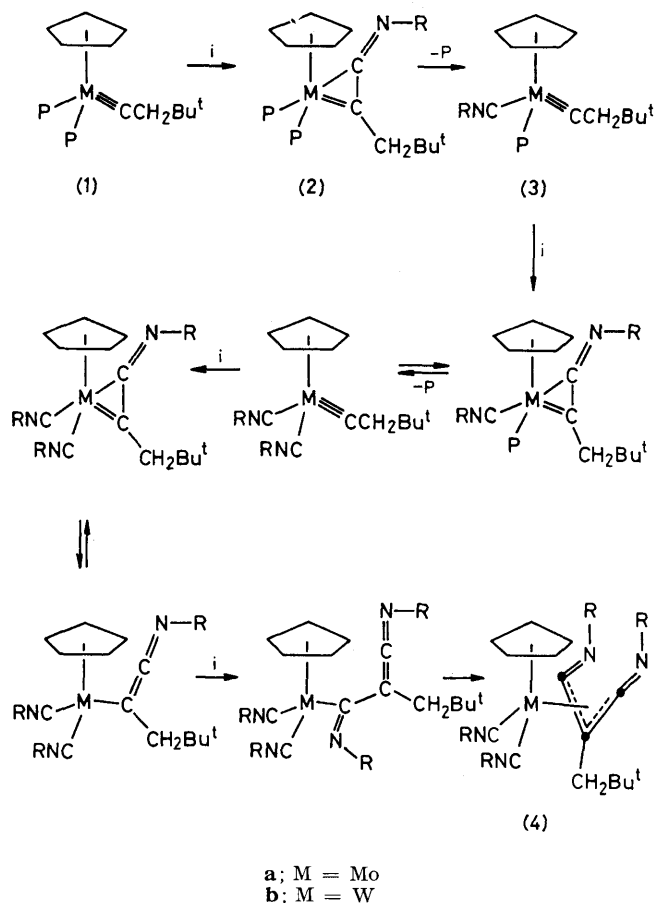
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*Summary* Reaction of alkylidyne complexes  $[M(CCH_2Bu^t)\{P(OMe)_3\}_2(\eta-C_5H_5)]$  ( $M = Mo, W$ ) with 2,6-xylyl isocyanide affords first  $[M(CCH_2Bu^t)(CN-2,6-Me_2C_6H_3)\{P(OMe)_3\}(\eta-C_5H_5)]$  then  $[M\{\eta^3-RN=C \cdots C(CH_2Bu^t) \cdots C=NR\}(CNR)_2(\eta-C_5H_5)]$  ( $R = 2,6-Me_2C_6H_3$ ), the molybdenum complex being identified by X-ray crystallography; in contrast, CO displaces the phosphite ligands

to give sequentially  $[Mo(CCH_2Bu^t)(CO)\{P(OMe)_3\}(\eta-C_5H_5)]$  and  $[Mo(CCH_2Bu^t)(CO)_2(\eta-C_5H_5)]$ .

THE development of new synthetic pathways to carbyne or alkylidyne complexes<sup>1,2,3</sup> provides stimulus for the development of this potentially rich area of chemistry. Our observation<sup>4</sup> and its generalisation,<sup>5</sup> that group 6 complexes

containing  $\sigma$ -bonded vinyl groups carrying a hydrogen atom on the carbon  $\alpha$  to the metal can rearrange to form electron rich alkyldiene complexes containing phosphite ligands, provided us with an opportunity to explore the reactions of these compounds with isocyanides and carbon monoxide.



SCHEME. i, 2,6-xylyl isocyanide (RNC). P=P(OMe)<sub>3</sub>.

In striking contrast with previous studies<sup>6</sup> of reactions of isocyanides with alkyldiene complexes, reaction (tetrahydrofuran, room temperature, 12 h) of [M(CCH<sub>2</sub>Bu<sup>t</sup>)<sub>2</sub>{P(OMe)<sub>3</sub>}<sub>2</sub>( $\eta$ -C<sub>6</sub>H<sub>5</sub>)] (1) (M = Mo, W) with 2,6-xylyl isocyanide afforded the orange crystalline complexes (4a and b)† in good yield. The structural identity of (4a) was established by a single crystal X-ray diffraction study at 23 °C. Crystals grown from n-hexane were found to contain a non-stoichiometric amount of solvent occluded in the lattice.

† Representative spectroscopic data for complexes (4a and b). Complex (4a)  $\nu_{\text{NC}}$  (hexane), 2 080s, 2 033s, 2 000sh, 1 730br. m, and 1 590 cm<sup>-1</sup>; <sup>13</sup>C n.m.r. (CDCl<sub>3</sub>, <sup>1</sup>H decoupled),  $\delta$  (p.p.m.), 205.4 (s,  $\dot{\text{C}}\text{NR}$ ), 189.3 (s, N=C $\cdots$ C $\cdots$ C=N), 153.2 (s, N=C $\cdots$ C $\cdots$ C=N). Complex (4b)  $\nu_{\text{NC}}$  (CH<sub>2</sub>Cl<sub>2</sub>), 2 087s, 2 035s, 1 999s, 1 663br. m, 1 623br. m., and 1 583s cm<sup>-1</sup>; <sup>13</sup>C n.m.r. (CDCl<sub>3</sub>, <sup>1</sup>H decoupled),  $\delta$  (p.p.m.), 177.2 (s,  $\dot{\text{C}}\text{NR}$ ), 173 (s, N=C $\cdots$ C $\cdots$ C=N), 154.4 (s, N=C $\cdots$ C $\cdots$ C=N).

‡ For M, D<sub>c</sub>, and F(000), the two values given correspond to population parameters of, respectively, 0.0 and 0.5 for the atoms of the relevant molecule. Since only half this molecule is, anyway, crystallographically unique, the respective complex to solvent ratios are 1:0.0 and 1:0.25.

§ Atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

¶ Supported by a search of the Cambridge Data Files.

Crystal data: (4a) C<sub>47</sub>H<sub>52</sub>MoN<sub>4</sub>.x C<sub>6</sub>H<sub>14</sub> (0.0 < x < 0.25), M = 768.9—790.4,‡ triclinc, a = 12.384(7), b = 17.669(8), c = 12.373(5) Å,  $\alpha$  = 99.79(4),  $\beta$  = 117.85(3),  $\gamma$  = 97.63(4)°, U = 2 287.7(18) Å<sup>3</sup>, Z = 2, D<sub>c</sub> = 1.116—1.147 g cm<sup>-3</sup>, F(000) = 808—833 electrons,  $\mu(\text{Mo-K}\alpha)$  = 2.7 cm<sup>-1</sup>, space group  $P\bar{1}$  from successful refinement.

Of 8 094 independent reflections measured to  $\theta_{\text{max}} = 25^\circ$  (graphite-monochromated Mo-K $\alpha$  X-radiation,  $\lambda = 0.710 69$  Å) on a Syntex P2<sub>1</sub> four-circle diffractometer, 6 025 had  $F \geq 2.0\sigma(F)$  and were used to solve (Patterson and Fourier techniques) and refine (full-matrix least-squares) the structure to a current R index of 0.105.§ This value and all molecular parameters discussed herein were obtained by assigning occupancy factors of 0.5 to atoms of the solvent molecule. Resulting U<sub>j</sub> values for these carbon atoms are relatively high (0.18—0.22 Å<sup>2</sup>) and probably indicate that the true occupancy is somewhat less.

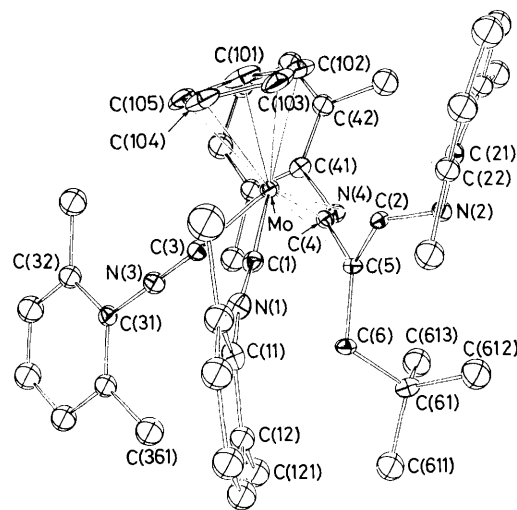


FIGURE. Molecular structure of (4a). Important distances include Mo—C(1) 2.051(9), C(1)—N(1) 1.171(11), Mo—C(3) 2.042(9), C(3)—N(3) 1.174(11), Mo—C(2) 2.155(8), Mo—C(5) 2.291(8), Mo—C(4) 2.158(9), Mo—C of C<sub>6</sub>H<sub>5</sub> 2.300(13)—2.358(11) Å.

The molecular geometry of (4a) and some important bond distances are given in the Figure. The complex has effective C<sub>s</sub> symmetry and an *endo* stereochemistry.<sup>7</sup> Parameters within the C<sub>6</sub>H<sub>5</sub> and  $\eta^1$ -(2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC) ligands are unexceptional, but the geometry and mode of coordination of the ally moiety are of considerable interest. To our knowledge¶ this study is the first structural characterisation of an allylic ligand where the terminal carbons are bound to only one other atom [the 2,6-dimethylphenylimino-nitrogens, N(2) and N(4)]. These nitrogen atoms are bent back away from the allylic plane to subtend C—C—N angles of 135.0(8) and 133.2(8)° (significantly more

bending of corresponding angles has been observed<sup>8</sup> in the complex  $[\text{Fe}(\text{CNBu}^t)_3\{1-4-\eta\text{-C}(\text{=N}^t\text{Bu}^t)=\text{C}(\text{Ph})\text{C}(\text{Ph})=\text{C}(\text{=N}^t\text{Bu}^t)\}]$ , and the adoption of transoid geometries about both C=N double bonds [C(2)=N(2) 1.284(10), C(4)=N(4) 1.270(11) Å] minimises intra-ligand steric congestion.

Although conforming to the effective mirror plane through the whole molecule the substituted allyl ligand is not evenly bonded to the metal, since the central carbon atom is tilted away such that Mo-C(central) exceeds Mo-C(terminal) by ca. 0.13 Å. In allyl complexes generally,<sup>9</sup> and  $[\text{M}(\text{allyl})\text{-L}_2(\eta\text{-C}_5\text{H}_5)]$  complexes specifically,<sup>10</sup> either the reverse pattern is observed, or else no significant difference in M-C lengths is found.<sup>11</sup> In (**4a**) it is probable that the tilting of the allyl fragment away from the molybdenum is due in part to the minimisation of intramolecular repulsive interactions between the  $\text{CH}_2\text{Bu}^t$  group pendant on C(5), and the aryl methyl groups of the  $\eta^1$ -bonded isocyanides. For the molecular structure as measured, the contacts C(611)...C(121), 3.79 Å, and C(611)...C(361), 3.95 Å, lie close to the accepted van der Waals sum.

N.m.r. spectral studies on reaction mixtures of  $[\text{Mo}(\text{CCH}_2\text{Bu}^t)\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$  and isocyanide are consistent with the build up, and then disappearance of, the monosubstituted alkyldiyne complex (**3**)  $[\text{Mo}(\text{CCH}_2\text{Bu}^t)(\text{CN}-2,6\text{-Me}_2\text{C}_6\text{H}_3)\{\text{P}(\text{OMe})_3\}(\eta\text{-C}_5\text{H}_5)]$  suggesting the possible importance of an initial rate determining loss of phosphite from the 18-electron bis-phosphite alkyldiyne complex (**1**). However, the observation that (**4a** and **b**) were formed at similar rates seemed to contradict this deduction, so the lability of the Mo-P bonds in  $[\text{Mo}(\text{CCH}_2\text{Bu}^t)\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$  was studied by <sup>31</sup>P{<sup>1</sup>H} n.m.r. spectroscopy. Spectra (in CD<sub>3</sub>C<sub>6</sub>D<sub>5</sub>) recorded at 100 °C in the presence of free P(OMe)<sub>3</sub> failed to show any broadening of the co-ordinated P(OMe)<sub>3</sub> signal; thus any exchange between free and co-ordinated phosphite was indicated to take longer than 0.5 s. An attempt was made to observe even slower exchange by applying the DANTE pulse sequence of Morris and Freeman.<sup>12</sup> In this experiment the spins of the free trimethyl phosphite were selectively inverted by a 180° pulse, and the spectrum was then

measured after a time  $t$  ( $0.1 < t < 2$  s). There was no evidence for any decrease in the intensity of the <sup>31</sup>P signal ( $\delta$  212.3 p.p.m., relative to H<sub>3</sub>PO<sub>4</sub>) of  $[\text{Mo}(\text{CCH}_2\text{Bu}^t)\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$  under these conditions (CD<sub>3</sub>C<sub>6</sub>D<sub>5</sub>, +100 °C), indicating that the half-time for the exchange must be greater than ca. 10 s at +100 °C. Thus the formation of (**4a** and **b**) at room temperature cannot involve initial loss of phosphite.

In spite of the stability of  $[\text{Mo}(\text{CCH}_2\text{Bu}^t)\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$  towards dissociative loss of phosphite, reaction (room temperature) with carbon monoxide displaces phosphite to give first the monocarbonyl alkyldiyne  $[\text{Mo}(\text{CCH}_2\text{Bu}^t)(\text{CO})\{\text{P}(\text{OMe})_3\}(\eta\text{-C}_5\text{H}_5)]$  [ $\nu_{\text{CO}}$  (hexane) 1 911s, 1 923sh cm<sup>-1</sup>] and then the dicarbonyl alkyldiyne  $[\text{Mo}(\text{CCH}_2\text{Bu}^t)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$  [ $\nu_{\text{CO}}$  (hexane) 1 998s, 1 928s cm<sup>-1</sup>; <sup>13</sup>C n.m.r. (C<sub>6</sub>D<sub>6</sub>), <sup>1</sup>H decoupled,  $\delta$  (p.p.m.) 332.8 (s, Mo≡C), 229.8 (s, MoCO), 92.4 (C<sub>5</sub>H<sub>5</sub>), 64.8 (s, CH<sub>2</sub>), 33.2 (s, CMe<sub>3</sub>), 29.5 (s, CMe<sub>3</sub>); <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>),  $\delta$  5.04 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 2.15 (s, 2 H, CH<sub>2</sub>), and 0.94 (s, 9 H, CMe<sub>3</sub>). Synthetically this reaction provides an interesting link with the complexes obtained by the Munich group<sup>13</sup> from carbene complexes. However, the problem remains as to how carbon monoxide and 2,6-xylyl isocyanide can effectively displace trimethyl phosphite under mild conditions.

It is suggested that this occurs *via* a novel cheletropic<sup>14</sup> reaction involving a concerted attack by CO<sup>15</sup> or RNC on the metal-carbon triple bond, a reaction which is thermally allowed since the  $[\text{ML}_2(\eta\text{-C}_5\text{H}_5)]$  (M = Mo, or W) fragment<sup>7,16</sup> is isolobal with CR. As is illustrated in the Scheme for the reaction with isocyanide this leads to the formation of a metallacycloprenimine,<sup>17</sup> which can rearrange with loss of phosphite or alternatively open to form a  $\eta^1$ -bonded iminoketenyl complex, which, *via* migration onto co-ordinated isocyanide, affords the  $\eta^3$ -bonded complexes (**4a** and **b**). It is interesting that in the reaction with CO the oxygen analogues of (**4a** and **b**) are not formed.

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<sup>6</sup> In contrast, *t*-butyl isocyanide simply displaces CO from the neutral complex  $[\text{trans-BrM}(\text{CC}_6\text{H}_5)(\text{CO})_4]$  (E. O. Fischer, A. R. Ruhs, and F. R. Kreissl, *Chem. Ber.*, 1977, **110**, 805), and forms an unstable ionic species  $[\text{Mn}\{\text{C}(\text{C}_6\text{H}_5)\text{CN}^t\text{Bu}^t\}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4^-]$  with the cationic alkyldiyne complex  $[\text{Mn}(\text{CC}_6\text{H}_5)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4^-]$  (E. O. Fischer, W. Schambeck, and F. R. Kreissl, *J. Organomet. Chem.*, 1979, **169**, C27).

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<sup>9</sup> See, for example, F. A. Cotton and J. Takats, *J. Am. Chem. Soc.*, 1968, **90**, 2031; F. Dawans, J. Dewailly, J. Meunier-Piret, and P. Piret, *J. Organomet. Chem.*, 1974, **76**, 53.

<sup>10</sup> G. Huttner, H. H. Brintzinger, L. G. Bell, P. Friedrich, V. Bejerke, and D. Neugebauer, *J. Organomet. Chem.*, 1978, **145**, 329; M. Green, J. Z. Nyathi, C. Scott, F. G. A. Stone, A. J. Welch, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1978, 1067.

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<sup>12</sup> G. A. Morris and R. Freeman, *J. Magn. Reson.*, 1978, **29**, 433.

<sup>13</sup> E. O. Fischer and U. Schubert, *J. Organomet. Chem.*, 1975, **100**, 59.

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<sup>15</sup> The reverse reaction is well known in which acetylenes can be prepared by thermolysis of cyclopropenones, see C. Wilcox and R. Breslow, *Tetrahedron Lett.*, 1980, **21**, 3241, and references therein.

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<sup>17</sup> Both a metallacycloprenone (M. Green, N. C. Norman, and A. G. Orpen, *J. Am. Chem. Soc.*, 1981, **103**, 1267) and a metallacycloprenone (W. Vedelhoven, K. Eberl, and F. R. Kreissl, *Chem. Ber.*, 1979, **112**, 3376) have been structurally characterised, supporting the suggestion that an intermediate of this type could be involved.