Stable Anionic η^1-Vinylidene Complexes of Molybdenum and Tungsten

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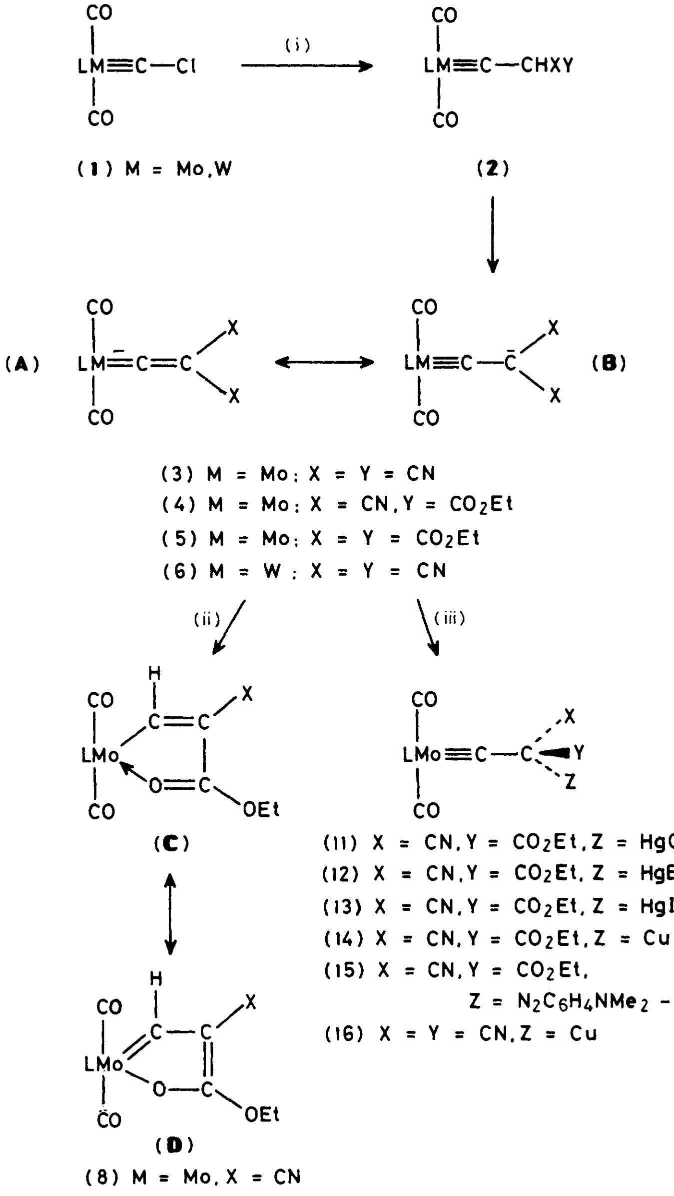
Secondary carbanions $[CHXY]^-$ (X,Y = CN, CO_2Et) react with the η^1-chlorocarbyne ligand in $[L(CO)_2M{\equiv}CCl]$ [L = hydrotris(3,5-dimethylpyrazol-1-yl)borate, M = Mo, W] to yield the first isolable anionic group 6 η^1-vinylidene complexes $[L(CO)_2M(C{\cdot}CXY)]^-$ and reaction of the latter (M = Mo, X = CN or CO_2Et, Y = CO_2Et) with a variety of electrophilic or oxidising reagents yields in each case a single neutral product, one example of which has been crystallographically characterised as the 7-co-ordinate oxametallacyclic carbene complex $[L(CO)_2\overline{M{=}CH{\cdot}C(CN){=}C(OEt)O}]$; in contrast HgX_2, CuI, and $[ArN_2]BF_4$ yield novel highly functionalised carbyne complexes $[L(CO)_2M{\equiv}C{\cdot}C(CN)(CO_2Et)(Z)]$ where Z = HgX, Cu, and N_2Ar respectively.

The synthesis and interconversion of mononuclear group 6 transition metal complexes containing highly unsaturated C_2 ligands (*e.g.* ethyne, ethynyl, vinyl, vinylidene, and ethylidyne or their substituted derivatives) is the subject of much current interest.[1—5] We recently described the preparation of group 6 complexes containing the unique chlorocarbyne ligand, *i.e.* $[M{\equiv}CCl(CO)_2L]$ [**1**, M = Mo, W; L = hydrotris(3,5-dimethylpyrazol-1-yl)borate = $HB(C_5H_7N_2)_3$][6] and demonstrated that nucleophilic substitution at the carbyne carbon in (**1**) affords a promising synthetic route to unusual ligand structures.[7] We now describe the utility of complex (**1**) as the starting point for a potentially versatile synthetic methodology for the *in situ* construction of Mo- or W-complexed *C*-substituted vinylidene ligands.

The sodium salts of the moderately strong CH acids CH_2XY (X,Y = CN, CO_2Et) react smoothly with (**1**) (Scheme 1) to give yellow–orange anionic η^1-vinylidene complexes $[M(C{\cdot}CXY)(CO)_2L]^-$ (**3**—**6**),† conveniently isolated in up to 97% yield as salts with quaternary ammonium cations. The ease with which the reaction proceeds is increased by progressive substitution of CN for CO_2Et in the carbanion: generation of (**5**) requires 72 h in refluxing tetrahydrofuran (THF) while formation of (**3**) is essentially complete within *ca.* 2.5 h at room temperature. To our knowledge compounds (**3**—**6**) are the first isolable anionic group 6 η^1-vinylidene complexes. A closely related anion, $[Mo(C{\cdot}CHBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]^-$ (**7**), has been detected in solution but this very labile species is rapidly protonated by water yielding a neutral carbyne complex.[2] Complexes (**3**—**6**) do not react with water and their increased stability *vis-à-vis* (**7**) is undoubtedly due to the ability of the electron-withdrawing groups X and Y to increase the contribution of the carbyne resonance form (**B**) to the ground state of the anion (Scheme 1). We presume that formation of (**3**—**6**) proceeds *via* deprotonation of the neutral carbyne complex (**2**) (Scheme 1) but intervention of the latter could not be detected by i.r. spectroscopy and reaction of a 1:1 mixture of $Na[CH(CN)CO_2Et]$ and (**1**) yields only (**4**) and starting material.

$$[Mo(C{\cdot}CHBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]^-$$
(**7**)

Although the charge on the labile anionic vinylidene complex (**7**) is thought to reside largely on the molybdenum atom its chemical behaviour is dominated by β-carbon



Scheme 1. L = $HB(C_5H_7N_2)_3$. *Reagents*: (i) Na[CHXY] (3 equiv.), THF; (ii) (**8**): 10% aq. $HCl\text{–}CH_2Cl_2$, (93%); PhCOCl, MeCN (80%); $[(\eta\text{-}C_5H_5)_2Fe]BF_4$, MeCN (50%); $[Ph_2I]PF_6$, CH_2Cl_2 (23%); NaOCl, aq. $NaOH\text{–}CH_2Cl_2$ (30%), $CoCl_2$, anhydr. MeCN, then H_2O (90%); (**9**): 10% aq. $HCl\text{–}CH_2Cl_2$ (50%); $[(\eta\text{-}C_5H_5)_2Fe]BF_4$, MeCN (50%); (iii) (**11**—**13**): HgX_2 (2—3 equiv.), CH_2Cl_2, 80%; (**14**, **16**): CuI, MeCN (90%); (**15**) $[p\text{-}Me_2NC_6H_4N_2]BF_4$, THF, −20 °C, 40%.

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† Correct microanalytical data have been obtained for all new compounds. *Selected spectroscopic data* for (**4**): i.r. (KBr), $\nu(CN)$ 2165m cm^{-1}: $\nu(CO)$ 1948, 1844s cm^{-1}; $\nu(CO)_{ester}$ 1636m cm^{-1}; ^{13}C n.m.r. ($CDCl_3$) δ 299.86 [s, $MoC{\cdot}C(CN)(CO_2Et)$], 229.27 [s, *C*O], 171.61 [s, $MoC{\cdot}C(CN)(CO_2Et)$], 123.94 [s, $MoC{\cdot}C(CN)(CO_2Et)$], 86.82 [s, $MoC{\cdot}C(CN)(CO_2Et)$].

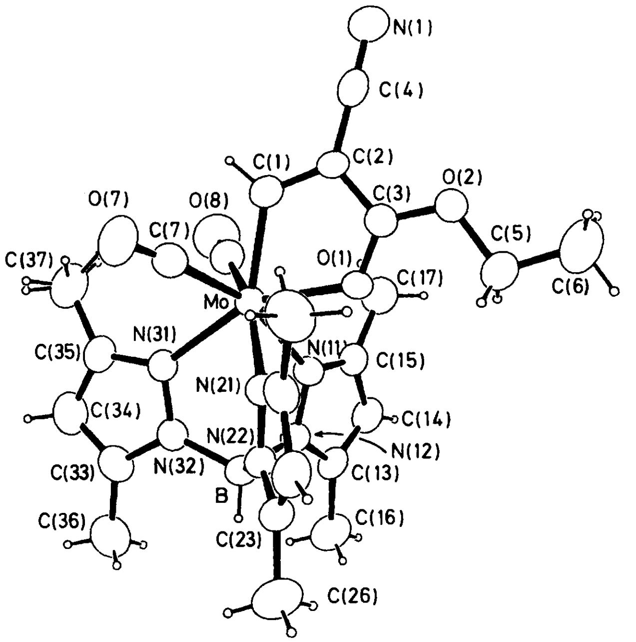

Figure 1. Molecular structure of (**8**): key dimensions are Mo–O(1) 2.133(2), Mo–C(1) 2.085(3), Mo–C(7) 1.977(3), Mo–C(8) 1.972(3), Mo–N(11) 2.214(2), Mo–N(21) 2.214(2), Mo–N(31) 2.213(2), C(1)–C(2) 1.383(4), C(2)–C(3) 1.401(4), C(2)–C(4) 1.429(4), C(3)–O(1) 1.255(3), C(3)–O(2) 1.327(4), C(4)–N(1) 1.141(4) Å. The hydrogens on methyl carbon C(37) are disordered equally over two sites.

nucleophilicity and/or susceptibility to oxidative dimerisation leading to the formation of neutral carbyne complexes.[1,2] An even more pronounced β-*C* nucleophilicity might be anticipated for the Mo compounds (**3**—**5**) but the chemical behaviour of these species is more complex than a simple comparison with (**7**) might suggest. Treatment of (**4**) with HCl or PhCOCl, with the oxidants $[(\eta\text{-}C_5H_5)_2Fe]BF_4$, $[Ph_2I]PF_6$, and NaOCl or with $CoCl_2$ gave in each case the same single yellow complex (**8**) as the major or only carbonyl-containing product. Similar behaviour is observed for (**5**) (Scheme 1) but not for (**3**) (see below).

The spectroscopic properties of (**8**), particularly the absence of an ester ν(CO) band in its i.r. spectrum, suggested a major alteration in molecular architecture and prompted a single-crystal *X*-ray diffraction study.‡ A view of the molecule of (**8**) (ORTEP,[8] SDP-plus[9]) is shown in Figure 1 and important metrical parameters are given in the caption. The complex contains a five-membered $\overline{MoC_3O}$ ring produced by formal protonation of the α-C of the vinylidene ligand in (**4**) with concommitant redistribution of electron density and bond-formation between the carbonyl oxygen of the original ester group in (**4**) and the molybdenum atom. The Mo atom is 7-co-ordinate. Both vinyl ketone (**C**) and prop-1-ene-1-oxy-3-ylidene (**D**) resonance forms may contribute to the ground state of the backbone of the chelating organic ligand in (**8**) (Scheme 1). Variously-substituted derivatives of the oxametallacyclic ring system present in (**8**) have been structurally characterised.[10—12] The Mo–C(1) distance in (**8**) [2.085(3) Å] is shorter than the 2.158(4) Å found for the analogous bond in the most closely comparable Mo complex $[(\eta\text{-}C_5H_5)(CO)_2\text{-}\overline{Mo{\cdot}C(Me){\cdot}C(Me){\cdot}C(R)O}]$ (**10**), R = (η-cyclopentadienyl)(dicarbonyl)molybdenum(η^3-1,1-dimethylpropen-3-yl)[10d] and falls within the range quoted for Mo–C double bonds.[13] In (**8**) the C(1)–C(2) and C(2)–C(3) distances differ by only 0.018 Å whereas (with a single exception[10a]) C(2)–C(3) is *ca.* 0.03—0.09 Å longer than C(1)–C(2) in all other examples of the MC_3O ring system for which structural data are available.[10b—f,11,12] These results suggest that the oxametallacyclic carbene structure (**D**) makes a more significant contribution to the ground state of (**8**) than is usual for this type of complex. In complex (**8**) the plane of the $\overline{MoC_3O}$ ring has been rotated by 90° from the 'piano-stool' geometry observed in the analogous η-cyclopentadienyl molybdenum complexes[10] so that it now lies on an approximate molecular mirror plane. Presumably this arrangement is adopted to minimise unfavourable interactions between the metallacyclic ring and the 3-methyl groups of the pyrazolylborate ligand. The Mo–C(1) bond of the five-membered ring is approximately normal to the plane of the pyrazolyl nitrogens N(11), N(21), and N(31).

The ubiquitous formation of (**8**) and (**9**) is most surprising given the established tendency of group 6 hydrotris(pyrazol-1-yl)borato complexes to avoid 7-co-ordination[13] and reaction conditions which would be expected[1,2] to lead to less sterically crowded 6-co-ordinated products. Cyclisation of (**4**) to (**8**) under acidic conditions may involve direct protonation at the vinylidene α-C analogous to the conversion of $[L(CO)_2W{\equiv}CSMe]$ to the chelated carbene complex $[L(CO)_2W(\eta^2\text{-}CH{\cdot}SMe)]^+$ reported by Angelici *et al.*[14] The mode of formation of (**8**) and (**9**) under oxidative conditions is presently less clear.

Contrasting chemical behaviour is shown when (**4**) is treated with HgX_2, CuI,§ or $[p\text{-}Me_2NC_6H_4N_2]^+$ when highly-coloured covalent 1:1 adducts of the anion with $[HgX]^+$ (**11**—**13**, scarlet), $[Cu]^+$ (**14**, orange), and $[p\text{-}Me_2NC_6H_4N_2]^+$ (**15**), purple) are formed in good yield (Scheme 1).¶ [Formation of (**15**) is accompanied by *ca.* 30% of (**8**).] The most reasonable structures for (**11**—**15**) involve formal replacement of the unique hydrogen atom in the carbyne ligand of (**2**) or on the carbene carbon of (**8**) by HgX, Cu, or N_2Ar respectively. The dicyanovinylidene anion (**3**) cannot cyclise to a carbene complex analogous to (**8**) but nonetheless forms a stable orange Cu^I adduct (**16**) with properties very similar to those of (**14**).¶ We conclude that complexes (**11**—**16**) are novel highly-functionalised carbyne complexes produced by electrophilic attack of the relevant reagent at the β-C of vinylidene ligand. For (**11**—**14**) the very low-frequency ester carbonyl bands¶ suggest associated structures bridged *via* donation from ester carbonyl to Hg or Cu. A similar μ-cyano structure is likely for (**16**).

Preliminary studies indicate that (**1**) reacts with a wide variety of other carbanionic species and these reactions,

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‡ *Crystal data for* (**8**): $C_{23}H_{28}BMoN_7O_4$, M = 573.3, monoclinic, space group $P2_1/n$, a = 19.379(3), b = 10.453(3), c = 13.246(3) Å, β = 98.77(2)°. U = 2652(2) Å^3, Z = 4, D_c = 1.44 g cm^{-3}. $F(000)$ = 1176, T = 293 K. λ = 0.71073 Å, $\mu(\text{Mo-}K_\alpha)$ = 5.2 cm^{-1}. Data were collected with an Enraf-Nonius CAD-4 diffractometer and corrected for Lorentz, polarisation, and absorption factors. All hydrogens were located and included, but not refined, in the full-matrix least-squares refinement.[9] At convergence R was 0.029 (R_w = 0.039) for 3870 observed reflections with 2° < θ < 28°. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.

§ The more labile anion (**7**) is oxidatively dimerised to a bis-carbyne complex by this reagent.[1]

¶ I.r., (**11**) (KBr) ν(CN) 2190s cm^{-1}, ν(CO) 2011, 1940vs cm^{-1}, $\nu(CO)_{ester}$ 1595m cm^{-1}; (**14**) (Nujol) ν(CN) 2210s cm^{-1}, ν CO) 1989, 1898, 1885vs cm^{-1}, $\nu(CO)_{ester}$ 1573m cm^{-1}; (**15**) (KBr) ν(CN) 2202s cm^{-1}, ν(CO) 2015, 1940vs cm^{-1}, $\nu(CO)_{ester}$ 1688m cm^{-1}; (**16**) (Nujol) ν(CN) 2202, 2180s cm^{-1}, ν(CO) 1975, 1892vs cm^{-1}.

together with the chemistry of the new species described here, are undergoing further investigation.

We thank the Natural Sciences and Engineering Research Council of Canada for financial support to G. F.

Received, 5th July 1988; Com. 8/02668H

References

1 R. G. Beevor, M. J. Freeman, M. Green, C. E. Morton, and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1985, 68.

2 D. S. Gill and M. Green, *J. Chem. Soc., Chem. Commun.*, 1981, 1037.

3 P. K. Baker, G. K. Barker, M. Green, and A. J. Welch, *J. Am. Chem. Soc.*, 1980, **102**, 7811.

4 R. G. Beevor, M. Green, A. G. Orpen, and I. D. Williams, *J. Chem. Soc., Dalton Trans.*, 1987, 1319; S. R. Allen, R. G. Beevor, M. Green, A. G. Orpen, K. E. Paddick, and I. D. Williams, *ibid.*, 1987, 591; J. S. Adams, M. Cunningham, and M. W. Whiteley, *J. Organomet. Chem.*, 1985, **293**, C13; A. Mayr, K. C. Schaefer, and E. Y. Huang, *J. Am. Chem. Soc.*, 1984, **106**, 1517; K. R. Birdwhistell, S. J. Nieter Burgmayer, and J. L. Tempelton, *ibid.*, 1983, **105**, 7789; R. G. Beevor, M. Green, A. G. Orpen, and I. D. Williams, *J. Chem. Soc., Chem. Commun.*, 1983, 673.

5 M. I. Bruce and A. G. Swincer, *Adv. Organomet. Chem.*, 1983, **22**, 60.

6 T. Desmond, F. J. Lalor, G. Ferguson, and M. Parvez, *J. Chem. Soc., Chem. Commun.*, 1983, 457.

7 T. Desmond, F. J. Lalor, G. Ferguson, and M. Parvez, *J. Chem. Soc., Chem. Commun.*, 1984, 75.

8 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee (1976).

9 B. Frenz and Associates, Inc., SDP-Plus, College Station, Texas 77840 and Enraf-Nonius, Delft, Holland (1983).

10 (a) E. R. Burkhardt, J. J. Doney, R. G. Bergman, and C. H. Heathcock, *J. Am. Chem. Soc.*, 1987, **109**, 2022 and references therein; (b) H. G. Alt, G. S. Herrmann, H. E. Englehardt, and R. D. Rogers, *J. Organomet. Chem.*, 1987, **331**, 329; (c) B. J. Brisdon, D. W. Brown, C. R. Willis, and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1986, 2405; (d) M. Green, R. C. Mercer, A. G. Orpen, C. J. Schaverien, and I. D. Williams, *J. Chem. Soc., Dalton Trans.*, 1986, 1971; (e) H. G. Alt, H. E. Englehardt, U. Thewalt, and J. Riede, *J. Organomet. Chem.*, 1985, **288**, 165; (f) N. E. Kolobova, I. L. Ivanov, O. S. Zhvanko, A. S. Batsanov, and Yu. T. Strutchkov, *ibid.*, 1985, **279**, 419.

11 W. A. Herrmann, M. L. Ziegler, and O. Serhadli, *Organometallics*, 1983, **2**, 958, and references therein.

12 H. Werner, R. Weinand, and H. Otto, *J. Organomet. Chem.*, 1986, **307**, 49.

13 M. D. Curtis, K-B. Shiu, and W. M. Butler, *J. Am. Chem. Soc.*, 1986, **108**, 1550 and references therein.

14 H. P. Kim, S. Kim, R. A. Jacobson, and R. J. Angelici, *Organometallics*, 1986, **5**, 2481.