A New Carbyne Ligand; Synthesis of Novel M^{IV} (M = Mo, W) Complexes containing Terminal Halogenomethylidyne Ligands: *X*-Ray Crystallographic Characterisation of η^1-Chloromethylidyne(dicarbonyl)-[tetrakis(1-pyrazolyl)borato]molybdenum(IV)

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Oxidation of the poly(1-pyrazolyl)borato complexes $[M(CO)_3\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]^-$ (M = Mo, W) with either $[ArN_2]^+$ (Ar = aryl) or $[Ph_2I]^+$ in the presence of a source of dihalogenoalkyl radicals leads to the formation of the η^1-halogenomethylidyne complexes $[Mo(\eta^1\text{-}CX)(CO)_2\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]$ (X = Cl, Br, and I) and $[W(\eta^1\text{-}CCl)(CO)_2\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]$; a closely related complex, $[Mo(\eta^1\text{-}CCl)(CO)_2\{B(C_3H_3N_2)_4\}]$ has been characterised by *X*-ray crystallographic methods.

In an earlier communication[1] we showed that the reaction of tricarbonyl (group 6B metal)[hydrotris(3,5-dimethyl-1-pyrazolyl)borato] anions $[M(CO)_3\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]^-$, (**1**, M = Mo, W) with $[ArN_2]^+$ (Ar = aryl) or $[Ph_2I]^+$ in MeCN or Me_2CO proceeds *via* redox and radical coupling to yield novel M^{II} η^2-aroyl complexes $[M(\eta^2\text{-}COAr)(CO)_2\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]$ (**2**). We now report that when this reaction is carried out using a suspension of (**1**) {as its $[Et_4N]^+$ salt} in CH_2Cl_2 only trace quantities of (**2**) are formed. Under these conditions the major product is a yellow-orange crystalline solid (**3**). The formation of (**3**) is independent of the oxidant employed but best yields (*ca.* 75%) were obtained using $[p\text{-}Me_2NC_6H_4N_2]^+$. Microanalytical and spectroscopic data were consistent with the formulation of (**3**) as novel η^1-chloromethylidyne derivatives of M^{IV}, *i.e.*, $[M(\eta^1\text{-}CCl)(CO)_2\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]$ (M = Mo, W).†

Since complexes containing terminal halogenomethylidyne ligands were unknown prior to this work, crystallographic verification of the proposed structure was desirable. Suitable crystals of (**3**) could not be obtained but we were able to produce good quality crystals of a closely related complex

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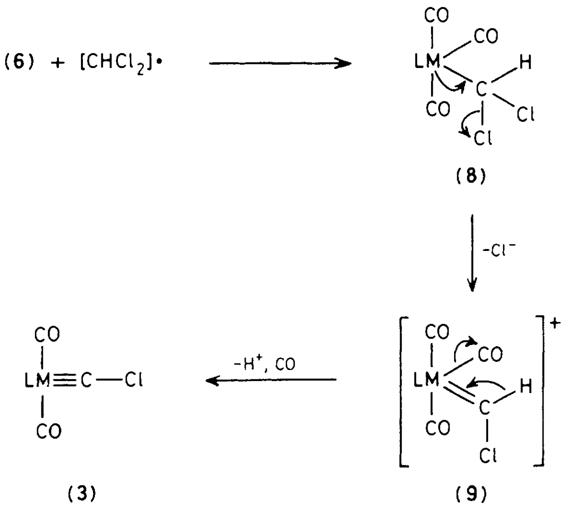
† Unless the contrary is stated correct microanalytical data were obtained for all new compounds described. Selected spectroscopic data for (**3**, M = Mo): ν(CO) (cyclohexane) 2005 and 1921vs cm^{-1}; ^{13}C n.m.r. ($CDCl_3$, Me_4Si) δ 224.03(CO) and 208.7 (methylidyne carbon) p.p.m.; mass spectrum, parent ion at *m/z* 498, prominent daughter ions at *m/z* 470 and 442.



Scheme 1. L = $[HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3]$; M = Mo, W.

$[Mo(\eta^1\text{-}CCl)(CO)_2\{B(C_3H_3N_2)_4\}]$ (**4**, $C_3H_3N_2$ = 1-pyrazolyl). Complex (**4**) was obtained in low yield from the tricarbonylmolybdenum[tetrakis(1-pyrazolyl)borato] anion, $[Mo(CO)_3\{B(C_3H_3N_2)_4\}]^-$, (**5**) by oxidation with $[Ph_2I]^+$ in CH_2Cl_2 solution.

Crystal data: $C_{15}H_{12}BClMoN_8O_2$, M_r = 478.5, triclinic, space group $P\bar{1}$, a = 14.425(3), b = 17.611(4), c = 11.634(3) Å, α = 101.85(2), β = 98.86(2), γ = 85.80(2)°, U = 2855.3 Å^3, Z = 6, D_c = 1.67 g cm^{-3}, 4531 observed reflections, R = 0.060.

Three-dimensional intensity data for (**4**) were collected with an Enraf–Nonius CAD-4 diffractometer and the structure was solved by the heavy-atom method and refined by least-squares calculations.‡ The unit cell of (**4**) contains three independent molecules, one of which is illustrated in Figure 1. Important parameters are given in the caption. The analysis confirmed the presence of the η^1-chloromethylidyne ligand in (**4**) and hence also in (**3**). Difference maps were computed on the basis of structure-factor calculations from which the O and Cl atom contributions had been omitted. The position of the chlorine atom in each molecule could then be determined uniquely from the peak height which was approximately twice that of the oxygen atom peaks. While crystals of (**4**) did not diffract strongly this analysis rules out the possibility of gross oxygen–halogen disorder of the kind which we have previously observed in related molecules of the type $[MX_2Y$(tridentate ligand)], *i.e.*, in $[RhI_2(CO)\{B(C_2H_3N_2)_4\}]$[2] and $[MoOCl_2\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]$,[3] although the presence of a small degree of oxygen–chlorine disorder in (**4**) cannot be entirely eliminated.

Our previous work[1] indicates that oxidation of (**1**) with $[ArN_2]^+$ or $[Ph_2I]^+$ in MeCN or Me_2CO leads initially to formation of an aryl radical together with the organometallic radical $[M(CO)_3\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]^\bullet$ (**6**). If the present reaction is carried out using 5% CH_2Cl_2 in cyclohexane as solvent and $[p\text{-}Me_2NC_6H_4N_2]^+$ as oxidant the yield of (**3**) drops from 75 to *ca.* 40% and is accompanied by a 25% yield of the η^2-acyl complex $[Mo(\eta^2\text{-}COC_6H_{11})(CO)_2\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]$ (**7**) indicating that radicals are also formed in this case.[1] A plausible mechanism for the subsequent formation of (**3**) is outlined in Scheme 1. Reaction of aryl radicals with CH_2Cl_2 generates the dichloromethyl radical[4] and we propose that the latter couples with (**6**) at the metal atom to yield the σ-dichloromethyl complex (**8**). α-Elimination of HCl from (**8**) [proceeding *via* the cationic chloromethylidene complex (**9**)] with expulsion of CO would then produce (**3**). We cannot exclude the possibility that the dichloromethyl radical reacts with (**6**) at a carbonyl carbon atom (as we have suggested elsewhere in the case of the cyclohexyl radical) but this pathway should generate an η^2-dihalogenoacetyl complex $[Mo(\eta^2\text{-}COCHCl_2)(CO)_2\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]$ (**10**) rather than (**3**).[1] Aryl radicals react with $CHBr_3$ and CHI_3 to produce the corresponding dihalogenoalkyl radicals[4] and treatment of (**1**, M = Mo) with $[Ph_2I]^+$ in $CHBr_3$ or in tetrahydrofuran containing

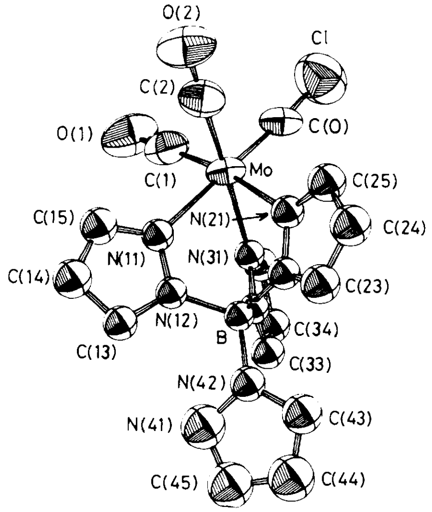


Figure 1. A perspective view of one of the independent molecules of (**4**). Principal bond lengths (Å) for the three independent molecules in sequence are: Mo–C(0) 1.894(9), 1.895(10), 1.894(10); Mo–C(1), 1.989(16), 2.003(14), 2.037(13); Mo–C(2) 2.009(12), 1.982(13), 1.977(12); Mo–N(11) 2.235(7), 2.250(7), 2.263(7); Mo–N(21) 2.231(7), 2.217(7), 2.212(8); Mo–N(31) 2.199(6), 2.191(7), 2.199(7); C(0)–Cl 1.539(11), 1.549(11), 1.552(10); C(1)–O(1) 1.442(16), 1.215(16), 1.146(17); C(2)–O(2) 1.222(15), 1.323(15), 1.168(15).

$[M(CO)_3\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]^-$
(**1**, M = Mo, W)
$[M(\eta^2\text{-}COAr)(CO)_2\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]$
(**2**, M = Mo, W)
$[Mo(\eta^1\text{-}CCl)(CO)_2\{B(C_3H_3N_2)_4\}]$
(**4**)
$[Mo(CO)_3\{B(C_3H_3N_2)_4\}]^-$
(**5**)
$[M(CO)_3\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]^\bullet$
(**6**, M = Mo, W)
$[Mo(\eta^2\text{-}COC_6H_{11})(CO)_2\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]$
(**7**)
$[Mo(\eta^2\text{-}COCHCl_2)(CO)_2\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]$
(**10**)
$[Mo(\eta^1\text{-}CX)(CO)_2\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]$
(**11**) **a**; X = Br
b; X = I

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‡ The atomic co-ordinates for this work 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.

an excess of CHI_3 yielded the η^1-bromomethylidyne and η^1-iodomethylidyne complexes $[Mo(\eta^1\text{-}CX)(CO_2)\{HB(3,5\text{-}Me_2\text{-}C_3HN_2)_3\}]$ (**11a**, X = Br; **11b**, X = I). Complex (**11b**) did not yield entirely satisfactory microanalytical data and was characterised spectroscopically.§

We are currently attempting to extend this synthesis of η^1-halogenomethylidyne complexes to other systems and are exploiting the chemical lability of the halogen in (**3**) and related complexes as a route to other novel group 6B complexes.

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§ I.r. (cyclohexane) (**11a**) ν(CO) 2008 and 1924vs cm^{-1}; (**11b**) ν(CO) 2009 and 1927vs cm^{-1}.