An Unusual Effect of Ligand Methyl-substitution in the Reaction of Tricarbonyl (Group 6A metal) [hydrotris(3,5-R_2-1-pyrazolyl)borato] Anions (R = H, Me) with Arenediazonium Cations: *X*-Ray Crystallographic Characterisation of a Mo^{II} η^2-Aroyl Complex, $[Mo(\eta^2\text{-}COC_6H_4Me\text{-}p)(CO)_2\{HB(3,5\text{-}Me_2C_3HN_2)_3\}]$ and of an η^2-Hexahydrobenzoyl Analogue, $[Mo(\eta^2\text{-}COC_6H_{11})(CO)_2\{HB(3,5\text{-}Me_2C_3HN_2)_3\}]$

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An *X*-ray crystallographic study has shown that the intensely-coloured products which result from the anomalous reaction of arenediazonium cations with $[Mo(CO)_3\{HB(3,5\text{-}Me_2C_3HN_2)\}_3]^-$ are η^2-aroyl dicarbonyl derivatives of Mo^{II}, $[Mo(\eta^2\text{-}COAr)(CO)_2\{HB(3,5\text{-}Me_2C_3HN_2)_3\}]$ rather than η^1-aryl tricarbonyl complexes as originally proposed: a by-product formed when the reaction is carried out in the presence of cyclohexane has been identified by *X*-ray crystallographic methods as the η^2-hexahydrobenzoyl complex $[Mo(\eta^2\text{-}COC_6H_{11})(CO)_2\{HB(3,5\text{-}Me_2C_3HN_2)_3\}]$ the formation of which has been interpreted in terms of a free-radical mechanism for the reaction.

Arenediazonium cations react with the Mo^0 poly-1-pyrazolylborato-complexes $[Mo(CO)_3\{RB(C_3H_3N_2)_3\}]^-$ (**1**) (R = H or $C_3H_3N_2$ = 1-pyrazolyl) to give red neutral CO-displacement products $[Mo(CO)_2(N_2Ar)\{RB(C_3H_3N_2)_3\}]$ (**2**).[1] In contrast, it has been reported that the reaction of a methyl-substituted analogue of (**1**), *i.e.* $[Mo(CO)_3\{HB(3,5\text{-}Me_2C_3HN_2)_3\}]^-$ (**3**) (3,5-$Me_2C_3HN_2$ ≡ 3,5-dimethyl-1-pyrazolyl) with $[ArN_2]^+$ in $HCONMe_2$ or CH_2Cl_2 proceeds with evolution of N_2 (rather than CO) and the formation of purple (Ar = C_6H_5) or blue (Ar = $C_6H_4NO_2$-*p*) products (**4**) in *ca.* 34% yield. An η^1-aryl Mo^{II} structure $[Mo(\eta^1\text{-}Ar)(CO)_3\{HB(3,5\text{-}Me_2C_3HN_2)_3\}]$ (**5**) was tentatively proposed for (**4**) but no definitive structural evidence was available.[2] Employing MeCN or Me_2CO as the reaction solvent and modifying the published work-up procedure has enabled us to prepare a wide range of complexes of type (**4**) from *o*-, *m*-, or *p*-substituted arenediazonium cations in reproducible yields of up to 75%. Several analogous tungsten complexes have also been synthesised but the reaction fails to produce any carbonyl-containing products when applied to the corresponding tricarbonylchromium anion. Complex (**4a**, Ar = C_6H_5) may also be prepared from (**3**) and $[(C_6H_5)_2I]^+$ in MeCN. Furthermore, if (**3**) is treated with $[p\text{-}NO_2C_6H_4N_2]^+$ in Me_2CO–cyclohexane (1 : 20) or with $[(C_6H_5)_2I]^+$ in MeCN–cyclohexane (1 : 20), formation of (**4**) is accompanied by a *ca.* 10% yield of a new red crystalline carbonyl complex (**6**).

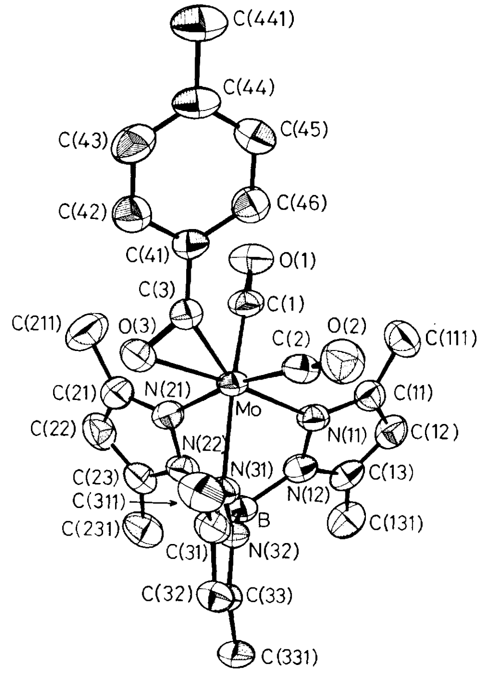

Figure 1. Molecular structure of (**4d**). Important dimensions [with corresponding values for (**6**) in square brackets]: Mo–C(3), 2.005(2) [1.996(9)]; Mo–O(3), 2.287(2) [2.291(6)]; C(3)–O(3), 1.245(3) [1.267(11)]; Mo–C(1), 1.959(3) [1.979(8)]; Mo–C(2), 1.953(3) [1.942(8)]; C(1)–O(1), 1.154(3) [1.148(10)]; C(2)–O(2), 1.164(3) [1.167(10)]; Mo–N(11), 2.199(2) [2.183(6)]; Mo–N(21), 2.242(2) [2.218(6)]; and Mo–N(31), 2.222(2) [2.272(6)] Å.

Microanalytical, i.r., mass spectroscopic, and n.m.r. (^{1}H and ^{13}C) data for (**4**) and the analogous tungsten complexes were compatible with the η^1-aryl formulation (**5**) originally proposed for the products of this reaction[2] and the data for (**6**) could be accommodated by an analogous η^1-cyclohexyl formulation, *i.e.* $[Mo(\eta^1\text{-}C_6H_{11})(CO)_3\{HB(3,5\text{-}Me_2C_3HN_2)_3\}]$ (**7**). However the colours of the complexes, which varied from deep red [(**4b**, Ar = $C_6H_4NMe_2$-*p*), (**6**)] to intense blue [(**4c**, Ar = $C_6H_4CF_3$-*p*)] were quite unexpected for complexes of this type. We therefore carried out an *X*-ray crystallographic analysis on a representative example of (**4**), (**4d**, Ar = C_6H_4Me-*p*), and on complex (**6**). Three-dimensional intensity data for (**4d**) and (**6**) were collected on an Enraf-Nonius CAD-4 diffractometer. The structures were solved by heavy-atom methods and refined by least-squares calculations.†

The molecular structure of (**4d**) is shown in Figure 1 and important dimensions [with corresponding values for (**6**) in square brackets] are listed in the caption. (The same crystallo-

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† *Crystal data:* (**4d**), $C_{25}H_{29}BMoN_6O_3$, M_r = 568.3, triclinic, space group $P\bar{1}$, a = 11.616(2), b = 12.811(2), c = 10.026(2) Å, α = 109.93(2), β = 108.78(2), γ = 88.26(1)°, U = 1322.6 Å^3, Z = 2, D_c = 1.42 g cm^{-3}, 4062 observed reflections, R 0.027; (**6**) $C_{24}H_{33}BMoN_6O_3$, M_r = 560.3, orthorhombic, space group $Pbn2_1$, a = 9.696(2), b = 16.039(7), c = 16.787(3) Å, U = 2610.9 Å^3, Z = 4, D_c = 1.43 g cm^{-3}, 1868 observed reflections, R 0.038. 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.

$[Mo(CO)_3\{RB(C_3H_3N_2)_3\}]^-$
(1)

$[Mo(CO)_2(N_2Ar)\{RB(C_3H_3N_2)_3\}]$
(2)

$[Mo(CO)_3\{HB(3,5\text{-}Me_2C_3HN_2)_3\}]^-$
(3)

$[Mo(\eta^2\text{-}COAr)(CO)_2\{HB(3,5\text{-}Me_2C_3HN_2)_3\}]$
(4) **a**: Ar = Ph
b: Ar = $C_6H_4NMe_2$-*p*
c: Ar = $C_6H_4CF_3$-*p*
d: Ar = C_6H_4Me-*p*

$[Mo(\eta^1\text{-}Ar)(CO)_3\{HB(3,5\text{-}Me_2C_3HN_2)_3\}]$
(5)

$[Mo(\eta^2\text{-}COC_6H_{11})(CO)_2\{HB(3,5\text{-}Me_2C_3HN_2)_3\}]$
(6)

$[Mo(\eta^1\text{-}C_6H_{11})(CO)_3\{HB(3,5\text{-}Me_2C_3HN_2)_3\}]$
(7)

$[Mo(CO)_3\{HB(3,5\text{-}Me_2C_3HN_2)_3\}]^\bullet$
(8)

graphic numbering-scheme is used for both complexes.) The analysis establishes that the Mo atoms in (**4d**) and (**6**) are 7-co-ordinate. Three co-ordination sites in each complex are occupied by the $[HB(3,5\text{-}Me_2C_3HN_2)_3]^-$ ligand and two by CO. The remaining two sites are occupied by a novel η^2-*p*-toluoyl ligand in (**4d**) and by an analogous η^2-hexahydrobenzoyl ligand in (**6**). To our knowledge the only previous report of a related structurally characterised Group 6A complex concerns the dimeric Mo^{II} η^2-acyl species $[MoCl(\eta^2\text{-}COCH_2SiMe_3)(CO)_2(PMe_3)_2]_2$.[3] The dimensions at Mo in the latter complex: Mo–C(acyl) 2.023(3), Mo–O(acyl) 2.292(2), and Mo–C(carbonyl) 1.940, 1.941(4) Å are very similar to those in (**4d**) and in (**6**). The short Mo–C(acyl or aroyl) bond lengths in all three complexes indicate significant d_π–p_π bonding between molybdenum and the carbon atom of the η^2-COR ligand.

It is well established that $[ArN_2]^+$ and $[Ar_2I]^+$ may interact with electron-rich substrates *via* a one-electron redox process which produces aryl radicals together with N_2 or ArI, respectively.[4] Such oxidation of (**3**) would simultaneously generate a 17-electron organometallic radical $[Mo(CO)_3\{HB(3,5\text{-}Me_2C_3HN_2)_3\}]^\bullet$ (**8**) formally analogous to the known[5] species $[Mo(CO)_3(\eta\text{-}C_5H_5)]^\bullet$. Coupling of the aryl radical with (**8**) would then produce (**4**). Strong evidence for the intermediacy of radical species in the oxidation of (**3**) with $[ArN_2]^+$ or $[Ar_2I]^+$ is provided by the isolation of the η^2-hexahydrobenzoyl complex (**6**). Formation of the latter is most reasonably explained by assuming hydrogen abstraction from cyclohexane by the aryl radical generated in the initial redox process followed by coupling of the resultant cyclohexyl radical with the organometallic radical (**8**). We incline to the view that (in this case at least) the radical coupling may take place directly at the carbon atom of a CO ligand rather than initially at the metal atom followed by migratory insertion of CO. The steric crowding evident in the co-ordination sphere of (**3**)[6]—and thus implied for the derived radical (**8**)—would be expected to militate against formation of an intermediate in which the bulky η^1-cyclohexyl group is directly bound to the metal atom, *e.g.* (**7**) (above).

It is clear that the methyl substituents in $[Mo(CO)_3\{HB(3,5\text{-}Me_2C_3HN_2)_3\}]^-$, (**3**), must play a critical role in diverting the course of the reaction with $[ArN_2]^+$ from the CO displacement pathway observed in their absence {*e.g.* with $[Mo(CO)_3\{RB(C_3H_3N_2)_3\}]^-$, (**1**)} to redox and radical arylation of co-ordinated CO with (**3**). Precisely how this unusual substituent effect operates is still far from clear and our current efforts are aimed at gaining a clearer understanding of the factors involved.

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