

Cyclopropanation in the reaction of $[\text{M}(\text{CO})_3\text{Tp}]^-$ [$\text{M} = \text{Mo}, \text{W}; \text{Tp} = \text{hydridotris}(\text{pyrazolyl})\text{borate}$] with $\text{I}(\text{CH}_2)_3\text{I}$ and the insertion of isocyanide into metal–acyl bonds

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Treatment of $\text{I}(\text{CH}_2)_3\text{I}$ with anions $[\text{M}(\text{CO})_3\text{Tp}]^-$ ($\text{M} = \text{Mo}, \text{W}$) leads to an η^2 -acyl cyclopropanation product $\text{M}(\text{CO})_2\{\eta^2\text{-C}(\text{O})(c\text{-C}_3\text{H}_5)\}\text{Tp}$ which decarbonylates to give π -allyl complexes and reacts with CNBu^t by formal insertion of isonitrile into the metal–acyl bond.

We have described earlier reactions between dihaloalkanes such as $\text{I}(\text{CH}_2)_3\text{I}$ and $[\text{M}(\text{CO})_n(\eta^5\text{-C}_5\text{H}_5)]^-$ ($n = 3, \text{M} = \text{Mo}, \text{W}; n = 2, \text{M} = \text{Fe}$) which lead to the formation of the cyclic carbene complexes $\text{M}(\text{CO})_{n-1}\{\text{C}(\text{CH}_2)_3\text{O}\}(\eta^5\text{-C}_5\text{H}_5)$.^{1,2} We are interested in these compounds in connection with their ability to act as precursors for compounds which undergo migrations to carbene. While examining related compounds but containing the hydridotris(pyrazolyl)borato (Tp) ligand, we discovered a remarkable cyclopropanation process and highly unusual insertions of isonitrile into metal acyl bonds.

The reaction between $[\text{W}(\text{CO})_3\text{Tp}]^-$ **1** with $\text{I}(\text{CH}_2)_3\text{I}$ affords small quantities of the η^2 -acyl cyclopropyl complexes $\text{W}\{\eta^2\text{-C}(\text{O})(c\text{-C}_3\text{H}_5)\}(\text{CO})_2\text{Tp}$ **2**. The η^2 -ligand is suggested by the solution IR spectrum ($\nu_{\text{CO}} 1958$ and 1824 cm^{-1}) which is typical of previously reported η^2 -acyl complexes.³ Other spectroscopic and spectrometric methods suggest the presence of the cyclopropyl group in complex **2**, but given that the few known cyclopropyl acyl complexes are formed from preconstructed cyclopropyl rings,⁴ it was felt necessary to confirm this unusual result by X-ray crystallography (Fig. 1). The cyclopropyl ring is orientated approximately perpendicular to the plane of the η^2 -acyl group while the η^2 -acyl group itself is best regarded as occupying a single coordination site of a slightly distorted octahedral tungsten. In the solid state, the acyl group does not lie on a mirror plane, and there is likely to be a low energy solution fluxional process as has been demonstrated *via* EHMO calculations on the complex $\text{Mo}\{\eta^2\text{-C}(\text{O})\text{Me}\}(\text{CO})_2\text{Tp}$ **3**. This process is described as a rapid net rocking motion of the acyl

group about the plane of symmetry which bisects the angle between the carbonyls and the two pyrazole groups *cis* to the acyl group.³

During the formation of **2**, monitoring by IR spectroscopy shows additional bands associated with the hydride $\text{WH}(\text{CO})_3\text{Tp}$ (by comparison with an authentic sample made by the analogous route known to give $\text{MoH}(\text{CO})_3\text{Tp}$).⁵ Further, IR and NMR evidence indicates the presence of the η^2 -acyl **4** in the reaction mixture. The inference that the anion $[\text{W}(\text{CO})_3\text{Tp}]^-$ acts as a base and removes a proton from the η^2 -acyl **4** (to give **5**) so inducing cyclization to give **2** is supported by the observation that addition of proton sponge [1,8-bis(dimethylamino)naphthalene] to the reaction mixture prevents the formation of $\text{WH}(\text{CO})_3\text{Tp}$ and increases the isolated yield of **2** to 74%. Therefore, the mechanism for cyclopropyl formation is believed to proceed (Scheme 1) *via* a deprotonation α to the acyl carbon and ring closure process. That the position α to the η^2 -acyl ligand in general is acidic is reinforced by earlier observations which show an α proton in complexes such as $\text{Mo}(\eta^2\text{-COMe})(\text{CO})_2\text{Tp}$ **3** is removed by base such as Bu^nLi or KH^6 and our finding that deprotonation of **2** with LDA followed by acidification or alkylation of the resulting anion affords the functionalized derivatives $\text{W}(\text{CO})_2\{\eta^2\text{-C}(\text{O})(c\text{-C}_3\text{H}_4\text{R})\}\text{Tp}$ (**6**, $\text{R} = \text{Me}$; **7** $\text{M} = \text{D}$; **8**, $\text{R} = \text{allyl}$). The corresponding reaction of the molybdenum anion $[\text{Mo}(\text{CO})_3\text{Tp}]^-$ **9** with $\text{I}(\text{CH}_2)_3\text{I}$ in the presence of proton sponge affords complex **10** (68%).

Complex **2** displays further interesting reactivity. Thermolysis or photolysis of **2** results in decarbonylation and ring opening of the cyclopropyl function to give the η^3 -allyl complex **11**.⁷ By way of partial comparison, an earlier report describes the ring opening of the cyclopropyl methyl complex $\text{Mo}(\text{CO})_3(\text{CH}_2\text{-}c\text{-C}_3\text{H}_5)(\eta\text{-C}_5\text{H}_5)$ in refluxing hexane to give the η^3 -allyl $\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_4\text{Me})(\eta\text{-C}_5\text{H}_5)$.⁸ Mechanistic insight into the formation of **11** in this way is given by the photolysis or thermolysis of the deuterated material $\text{W}(\text{CO})_2\{\eta^2\text{-C}(\text{O})(c\text{-C}_3\text{H}_4\text{D})\}\text{Tp}$ **7** which affords $\text{W}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_4\text{D})\text{Tp}$ **12** with > 95% deuterium labelling at the central carbon of the allyl group. Since no D-scrambling occurs, it is clear that the ring-opening process involves C–C bond cleavage between the two CH_2 groups and rearrangement to give **12**. The corresponding photolysis (but not thermolysis) of **6** affords the allyl derivative **13**.

Addition of CNBu^t to a solution of **2** in THF results in a remarkable reaction (48 h at ambient temperature for completion) leading to the α -keto- η^2 -iminoacyl **14** together with the seven-coordinate Tp tungsten η^1 -acyl complex **15**. There are examples of η^1 - α -ketoacyl complexes in the literature (however their formation is concurrent with oxidation at the metal centre⁹) and at least one example of a α -keto- η^1 -iminoacyl¹⁰ (but made from a pre-assembled ketoimidoyl group). Because of this unusual reaction, the structure of **14** was confirmed by X-ray crystallography (Fig. 2).[†] The iminoacyl bond length [C(12)–N(7) 1.257(14) Å] of **14** is in the range of those reported for other η^2 -iminoacyl complexes.¹¹ Stirring a solution of **15** in THF over three days results in only partial conversion of **14** with formation of unidentified decomposition products. Consequently, it may well be that in the reaction of **2** with CNBu^t to

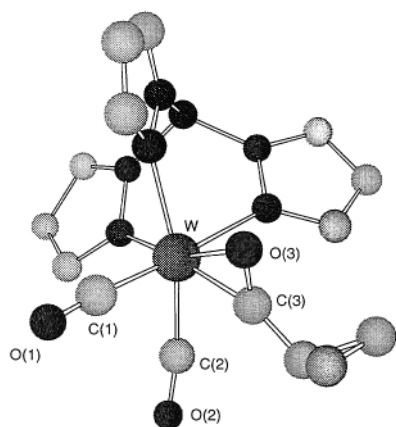
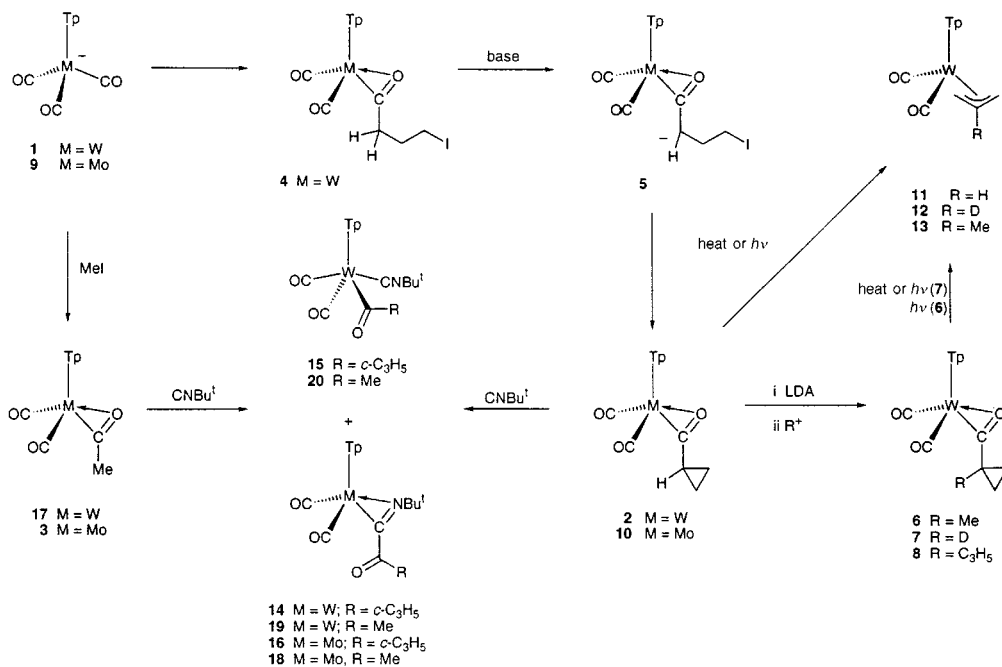
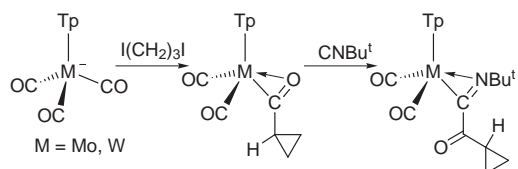


Fig. 1 Molecular structure of $\text{W}\{\eta^2\text{-C}(\text{O})(c\text{-C}_3\text{H}_5)\}(\text{CO})_2\text{Tp}$ **2**. Selected bond lengths (Å) and angles ($^\circ$), $\text{W}\text{-C}(3)$ 2.02(2), $\text{C}(3)\text{-O}(3)$ 1.25(2), $\text{O}(3)\text{-W}$ 2.217(10), $\text{C}(1)\text{-W}\text{-C}(2)$ 80.6(6), $\text{C}(3)\text{-W}\text{-O}(3)$ 34.0(4).



Scheme 1



Scheme 2

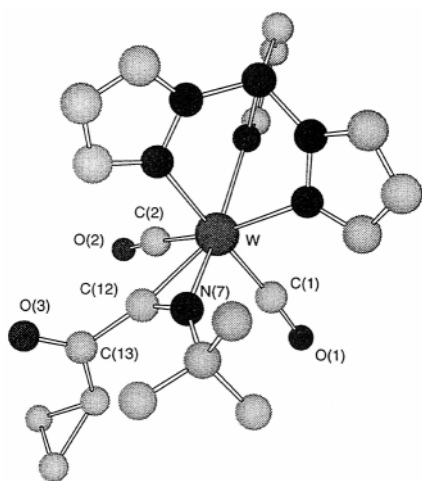


Fig. 2 Molecular structure of W{ η^2 -C(NBu^t)CO(*c*-C₃H₅)}(CO)₂Tp **14**. Selected bond lengths (Å) and angles (°), W–C(12) 2.101(11), C(12)–N(7) 1.257(14), N(7)–W 2.190(8), C(1)–W–C(2) 80.0(5), C(12)–W–N(7) 34.0(4).

form **14**, a route *via* **15** is not the major path leading to **14**. The insertion of isonitrile into metal acyl bonds of this type is reasonably general. Thus, CNBu^t reacts with the molybdenum species **10** to form **16** and we also find that the complexes M{ η^2 -C(O)Me}(CO)₂Tp (**3**, M = Mo;³ **17** M = W) react with CNBu^t to give the insertion products M(CO)₂{ η^2 -C(NBu^t)-

(COR)}Tp (**18** M = Mo; **19**, M = W). In the tungsten case, the η^1 -acyl **20** is also isolable.

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Notes and references

† *Crystal data*: **2**: triclinic, space group $P\bar{1}(C_1^1$ no. 2) $a = 8.328(2)$, $b = 9.478(2)$, $c = 12.201(3)$ Å, $\alpha = 75.27(2)$, $\beta = 77.89(2)$, $\gamma = 74.17(2)^\circ$, $U = 885.8(4)$ Å³; $D_c = 1.957$ g cm⁻³, $Z = 2$. Mo-K α radiation ($\lambda = 0.71073$ Å), $\mu(\text{Mo-K}\alpha) = 6.548$ mm⁻¹, $F(000) = 500$. Data were collected in the range $3.5 < 2\theta < 45^\circ$ (ω -scan), 2024 independent reflections [$|F|/\sigma(F) > 4.0$], final $R = 0.0546$, with allowance for the thermal anisotropy of all non-hydrogen atoms.

14, monoclinic, space group $P2_1/n$ [a non standard setting of $P2_1/c$ (C_{2h}^5 , no. 14), $a = 8.016(2)$, $b = 36.229(7)$, $c = 9.501(2)$ Å, $\beta = 112.84(3)^\circ$, $U = 2542.9(10)$ Å³; $D_c = 1.628$ g cm⁻³, $Z = 4$. Mo-K α radiation ($\lambda = 0.71073$ Å), $\mu(\text{Mo-K}\alpha) = 4.581$ mm⁻¹, $F(000) = 1224$. Data were collected in the range $4.5 < 2\theta < 45^\circ$ (ω -scan), 2761 independent reflections [$|F|/\sigma(F) > 4.0$], final $R = 0.0449$ with allowance for the thermal anisotropy of all non-hydrogen atoms. CCDC 182/1162.

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