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Carbene complexes. Part 21. Synthesis and characterisation of bis(carbene)molybdenum(II) complexes and dimetal(0) complexes of the Group 6 elements containing novel bridging bis(carbene) ligands; X-ray structures of $[\text{Mo}(\text{CO})_2(\text{L}^{\text{Et}})_2(\text{OSO}_2\text{CF}_3)_2][\text{L}^{\text{Et}}=\text{CN}(\text{Et})(\text{CH}_2)_2\text{NEt}]$ and $[\text{W}(\text{CO})_5\{\text{C}(\text{OEt})\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}(\text{OEt})-\text{o}\}\text{W}(\text{CO})_5]$

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Abstract

Treatment of the bis(carbene)tetracarbonylmolybdenum (0) complex *cis*- $[\text{Mo}(\text{CO})_4(\text{L}^{\text{Et}})_2][\text{L}^{\text{Et}}=\text{[graphic omitted]Et}]$ with two equivalents of silver trifluoromethanesulphonate in tetrahydrofuran (thf) readily yields the molybdenum(II) complex $[\text{Mo}(\text{CO})_2(\text{L}^{\text{Et}})_2(\text{OSO}_2\text{CF}_3)_2]$ (**1**). Reaction of the complexes $[\text{M}(\text{CO})_6]$ (M = Cr or W) with $\text{Mg}[(\text{CH}_2)_2\text{C}_6\text{H}_4-\text{o}](\text{thf})$ (M = Cr) or *o*- $\text{C}_6\text{H}_4(\text{CH}_2\text{MgCl})_2$ (M = W) in thf affords the crystalline yellow μ -bis(carbene)-dimetal(0) complex $[\{\text{M}(\text{CO})_5\{\text{C}(\text{[graphic omitted]g}(\text{thf})_n\}[\text{M} = \text{Cr}, n = 3$ (**2a**); M = W, $n = 4$ (**2b**)]], which when extracted into water and treated with $[\text{Et}_3\text{O}][\text{BF}_4]$ furnishes the appropriate orange μ -bis(carbene) bimetallic complex $[\text{[graphic omitted]}(\text{OEt})\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{[graphic omitted]}(\text{CO})_5][\text{M} = \text{Cr}$ (**3a**) or W (**3b**)]. Complex (**3a**) with an excess of PEt_3 gives the red-orange complex $[\text{[graphic omitted]}(\text{OEt})\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{[graphic omitted]}(\text{CO})_4(\text{PEt}_3)]$. Reaction of $[\text{M}(\text{CO})_6]$ with *o*- $\text{C}_6\text{H}_4[\text{CH}(\text{SiMe}_3)\text{Li}(\text{tmen})]_2[\text{tmen} = \text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}_2]$ yields $[\text{[graphic omitted]}(\text{OLi}(\text{OEt}_2)(\text{tmen}))\text{CH}(\text{SiMe}_3)\text{C}_6\text{H}_4\text{CH}(\text{SiMe}_3)\text{[graphic omitted]}(\text{CO})_5]$. In the crystalline bis(carbene)-molybdenum(II) complex (**1**), the Mo atom resides at the centre of a severely distorted octahedron $[\text{C}_{\text{carb}}-\text{Mo}-\text{C}_{\text{carb}}\ 134.9(2)^\circ]$, with the two five-membered L^{Et} rings arranged so as to be approximately parallel, and mean lengths $\text{Mo}-\text{C}_{\text{carb}}\ 2.154(5)$, $\text{Mo}-\text{CO}\ 1.961(6)$, and $\text{Mo}-\text{O}\ 2.177(4)\text{\AA}$. In the crystalline ditungsten(0) complex (**3b**), each W is in an octahedral environment and selected mean parameters include $\text{W}-\text{C}_{\text{carb}}\ 2.155(12)$, $\text{W}-\text{CO}\ 2.03(4)$, and $\text{C}_{\text{carb}}-\text{O}\ 1.317(14)\text{\AA}$.