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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 $[Mo(CO)_2(L^{Et})_2(OSO_2CF_3)_2][L^{Et}{=}{=}CN(Et)(CH_2)_2NEt]$ and $[W(CO)_5\{C(OEt)CH_2C_6H_4CH_2C(OEt)\text{-}o\}W(CO)_5]$

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Abstract

Treatment of the bis(carbene)tetracarbonylmolybdenum (0) complex *cis*-$[Mo(CO)_4(L^{Et})_2][L^{Et}$= [graphic omitted]Et] with two equivalents of silver trifluoromethanesulphonate in tetrahydrofuran (thf) readily yields the molybdenum(II) complex $[Mo(CO)_2(L^{Et})_2(OSO_2CF_3)_2]$(**1**). Reaction of the complexes $[M(CO)_6]$(M = Cr or W) with $Mg[(CH_2)_2C_6H_4\text{-}o](thf)$(M = Cr) or $o\text{-}C_6H_4(CH_2MgCl)_2$(M = W) in thf affords the crystalline yellow μ-bis(carbene)-dimetal(0) complex [{$M(CO)_5$[C([graphic omitted]g$(thf)_n$][M = Cr, *n*= 3 (**2a**); M = W, *n*= 4 (**2b**)], which when extracted into water and treated with $[Et_3O][BF_4]$ furnishes the appropriate orange μ-bis(carbene) bimetallic complex [[graphic omitted](OEt)$CH_2C_6H_4CH_2$[graphic omitted]$(CO)_5$][M = Cr (**3a**) or W (**3b**)]. Complex (**3a**) with an excess of PEt_3 gives the red-orange complex [{[graphic omitted](OEt)$CH_2C_6H_4CH_2$[graphic omitted]$(CO)_4(PEt_3)$}]. Reaction of $[M(CO)_6]$ with $o\text{-}C_6H_4[CH(SiMe_3)Li(tmen)]_2$[tmen = $Me_2N(CH_2)_2NMe_2$] yields [[graphic omitted]$OLi(OEt_2)$(tmen)]$CH(SiMe_3)C_6H_4CH$ $SiMe_3$][graphic omitted]$(CO)_5$]. In the crystalline bis(carbene)-molybdenum(II) complex (**1**), the Mo atom resides at the centre of a severely distorted octahedron [C_{carb}–Mo–C_{carb} 134.9(2)°], with the two five-membered L^{Et} rings arranged so as to be approximately parallel, and mean lengths Mo–C_{carb} 2.154(5), Mo–CO 1.961(6), and Mo–O 2.177(4)Å. In the crystalline ditungsten(0) complex (**3b**), each W is in an octahedral environment and selected mean parameters include W–C_{carb} 2.155(12), W–CO 2.03(4), and C_{carb}–O 1.317(14)Å.

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