Synthesis of Anionic Molybdenum and Tungsten Carbene Complexes of the Type $[M(carbene)(CO)_2(\eta\text{-}C_5H_5)]^-$ (M = Mo or W) by the Sodium Naphthalide Reduction of Iodo Carbene Complexes

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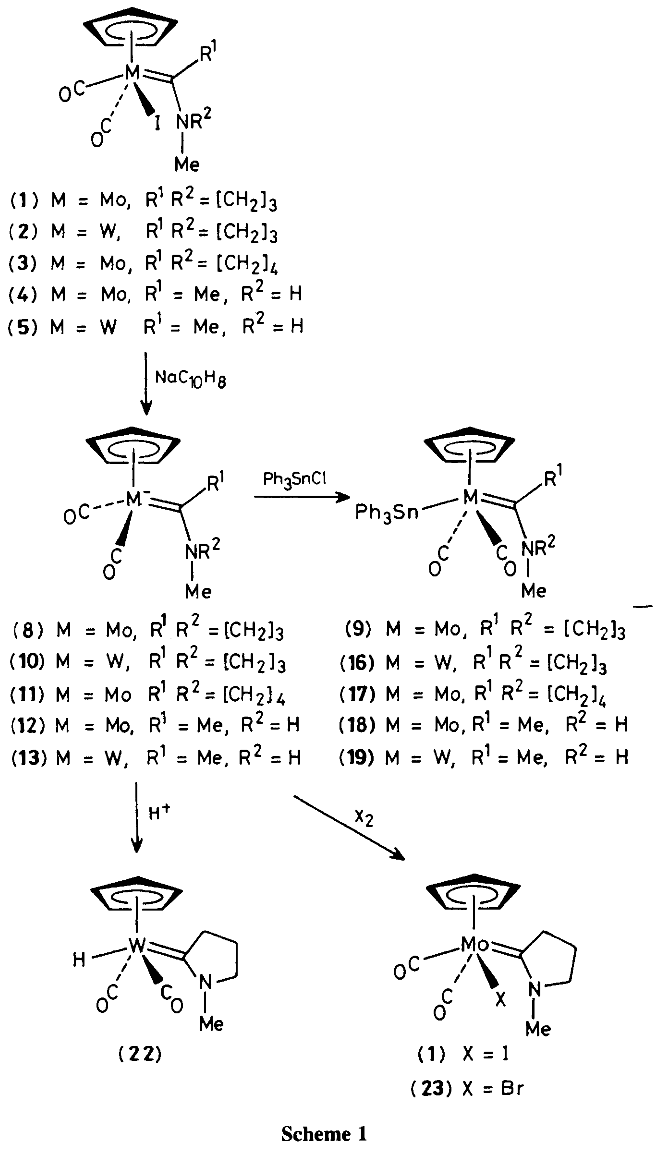
Addition of sodium naphthalide ($NaC_{10}H_8$) to solutions containing carbene complexes *trans*-$MI(CO)_2(=\overline{C[CH_2]_3O})(\eta\text{-}C_5H_5)$ (M = Mo or W), *cis*-$MI(CO)_2(=\overline{C[CH_2]_nN}Me)(\eta\text{-}C_5H_5)$ (M = Mo, n = 3 or 4; M = W, n = 3), or *cis*-$MI(CO)_2(=CMe[NHMe])(\eta\text{-}C_5H_5)$ (M = Mo or W) results in solutions containing the respective anionic carbene complexes $[M(carbene)(CO)_2(\eta\text{-}C_5H_5)]^-$, all of which react with Ph_3SnCl providing the appropriate tin derivatives *trans*-$M(SnPh_3)(carbene)(CO)_2(\eta\text{-}C_5H_5)$.

Nucleophilic carbene complexes of the type $[L_nM(carbene)]^-$ with a metal centred negative charge should be extremely useful synthons in organotransition metal chemistry but to our knowledge none has been reported. This type of anion is quite distinct from other anionic carbene complexes $Cr(=\overline{CCHLi[CH_2]_2O})(CO)_5$[1] or $Mn_2(=\overline{CCHLi[CH_2]_2O})(CO)_9$[2] with the general formula $L_nM(CR^1CH_2R^2Li)$ formed by proton abstraction from the carbon atom α to the carbene during treatment with alkyl lithium reagents. We now report syntheses of nucleophilic molybdenum and tungsten $[L_nM(carbene)]^-$ compounds.



Scheme 1

The carbene complexes (**1**)—(**7**) containing halide ligands may all be synthesised in reasonable to good yields[3] and we reasoned that sodium reduction of these compounds might lead to anionic carbene complexes by analogy with well known sodium reductions of, for instance, $MX(CO)_2L(\eta\text{-}C_5H_5)$ (M = Mo or W; L = CO, isonitrile, or PR_3; X = halide).[4]

Addition of just over two equivalents of sodium naphthalide,[5] $NaC_{10}H_8$, to a solution of (**1**) in tetrahydrofuran (thf) at −78 °C gives, after warming to ambient temperature, an air and moisture sensitive pale yellow solution whose i.r. spectrum [ν(CO) (thf); 1786s and 1666s cm^{-1}] is indicative of an anionic dicarbonyl species and assigned the structure (**8**) (Scheme 1). We find that $NaC_{10}H_8$ is a much more convenient reducing agent than sodium amalgam for this reaction. In addition, the overall yields are higher because of the lack of mercury containing side products.

Addition of 15-crown-5 to a solution containing the anion (**8**) results in changes to the i.r. spectrum [ν(CO) (thf); 1785s and 1673s cm^{-1}] in the carbonyl region. These changes are similar to those observed in the i.r. spectrum of $[Mo(CO)_2(P\{OPh\}_3)(\eta\text{-}C_5H_5)]^-$[6] and indicate that the anion exists exclusively as tight ion pairs with sodium ions in thf, with the sodium ion bound to the oxygen atom of a carbonyl group.

Assignment of the carbene anion structure (**8**) is suggested by the formation of the Ph_3Sn derivative (**9**). Addition of a slight excess of Ph_3SnCl to a solution containing (**8**) results in a solution with just two carbonyl i.r. bands [ν(CO) (thf); 1910m and 1838s cm^{-1}] corresponding to the only isolated product (**9**) (66%). Spectroscopic data† are very similar to those published for known related carbene complexes[3,7] and are in accord with the *trans* structure depicted. In particular a signal at δ 257.7 is in a position characteristic for complexes of the carbene $=\overline{C[CH_2]_3N}Me$. In addition the formulation (**9**) is confirmed by preliminary results of an *X*-ray crystallographic study.[8]

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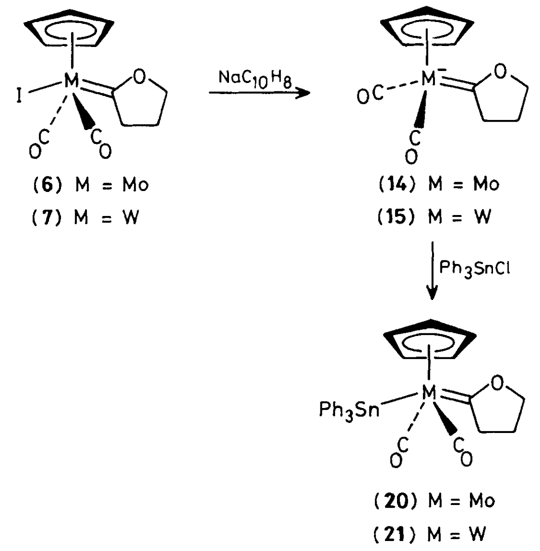
† *Selected spectroscopic data:* $Mo(SnPh_3)(=\overline{C[CH_2]_3N}Me)(CO)_2(\eta\text{-}C_5H_5)$, (**9**): mass [chemical ionisation, c.i. (NH_3)] *m/z* 651 $(M + 1)^+$; ν(CO) (CH_2Cl_2) 1908m and 1832s cm^{-1}; ^1H n.m.r., δ ($CDCl_3$) 7.61 (m, 6 H, Ph), 7.28 (m, 9 H, Ph), 5.22 (s, 5 H, C_5H_5), 3.64 (t, 2 H, *J* 8 Hz, CH_2), 3.40 (t, 2 H, *J* 8 Hz, CH_2), 3.08 (s, 3 H, Me), and 1.91 (quintet, 2 H, *J* 8 Hz, central CH_2); ^{13}C n.m.r., δ ($CDCl_3$, −50 °C) 257.7 (Mo=C), 233.5 (2CO), 144.8 (Ph), 136.8 (Ph), 127.6 (Ph), 90.4 (C_5H_5), 60.8 (CH_2), 55.1 (CH_2), 40.5 (Me), and 21.0 (central CH_2). $WH(=\overline{C[CH_2]_3N}Me)(CO)_2(\eta\text{-}C_5H_5)$, (**22**): mass [c.i. ($NH_3$)] *m/z* 388 $(M + 1)^+$; ν(CO) (CH_2Cl_2) 1924s and 1834s cm^{-1}; ^1H n.m.r., δ ($CDCl_3$) 5.29 (s, 5 H, C_5H_5), 3.64 [t, 2 H, *J*(HH) 7.5 Hz, CH_2], 3.46 (s, 3 H, Me), 3.14 [t, 2 H, *J*(HH) 7.5 Hz, CH_2], 1.84 [quintet, 2 H, *J*(HH) 7.5 Hz, central CH_2], and −7.11 [s, 1H, $J(^{185}W^1H)$ 39.5 Hz, W–H]; ^{13}C n.m.r., δ ($CDCl_3$, −40 °C) 241.9 (W=C), 224.6 (2CO), 88.6 (C_5H_5), 60.0 (CH_2), 54.4 (CH_2), 41.4 (Me), and 21.7 (central CH_2).



(6) M = Mo
(7) M = W
(14) M = Mo
(15) M = W
(20) M = Mo
(21) M = W

Scheme 2

In a similar fashion the related complexes (**2**)—(**7**) all react with $NaC_{10}H_8$ forming the respective anions (**10**)—(**15**) (Schemes 1 and 2). Their i.r. spectra are all similar suggesting a similar nature. In turn, each of (**10**)—(**15**) reacts with Ph_3SnCl to give the fully spectroscopically characterised tin derivatives (**16**)—(**21**), all of which have a *trans* geometry, in yields greater than 50%.

Further preliminary results show that the anions (**8**) and (**10**)—(**15**) are very reactive, especially with oxidising agents or proton sources. As examples, treatment of a solution containing (**10**) with $MeCO_2H$ gives the hydride (**22**) which is fully spectroscopically characterised.† The *trans* geometry is indicated by the relative intensities of the two carbonyl i.r. bands, the pairwise equivalence of the ring protons in the ^1H n.m.r. spectrum, and the presence of a single carbonyl resonance in the ^{13}C n.m.r. spectrum assigned to equivalent carbonyl groups. The hydride is manifested by a characteristic low frequency signal in the ^1H n.m.r. spectrum which also displays ^{185}W satellites. Addition of I_2 to a solution containing (**8**) results in incorporation of I^+ and reformation of the starting material (**1**), while addition of Br_2 to (**8**) gives the corresponding bromo carbene complex (**23**) whose spectroscopic properties, as expected, are qualitatively very similar to those of (**1**).

We thank the S.E.R.C. for substantial support and one of us (V.A.O.) is grateful for an S.E.R.C. research studentship.

Received, 19th August 1985; Com. 1230

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