

Synthesis of Heterobimetallic Telluro - Acyl Complexes

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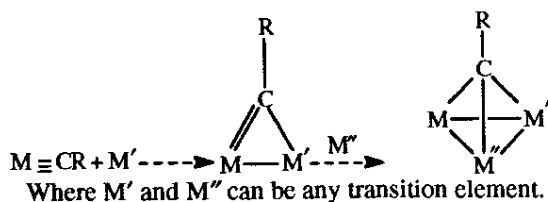
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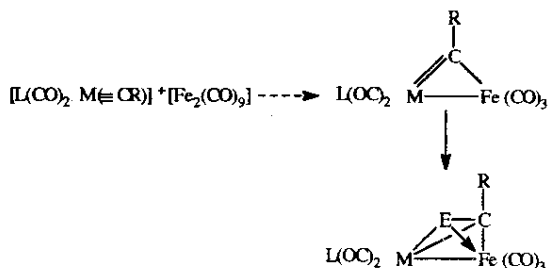
Summary: The μ -alkylidene dimetal complexes $[M Fe (\mu - C_6H_3Me_2 - 2,6) (CO)_5 (\eta - C_5H_5)]$, ($M = Cr, Mo$ or W) reacted with elemental tellurium yielding the heterobimetallic compounds $[M Fe (\mu - \eta^2 - Te CC_6H_3 Me_2 - 2,6) (CO)_5 (\eta - C_5H_5)]$. Similarly, the reaction between $[Mo Fe (\mu - CC_6H_4 Me - 4) (CO)_5 (\eta - C_5H_5)]$ and tellurium afforded the complex $[MoFe (\mu - \eta^2 - Te C C_6H_4 Me - 4) (CO)_5 (\eta - C_5H_5)]$.

Introduction

Compounds containing carbon to metal triple bonds, alkylidynes $[M(\equiv CR)(CO)_2L]$, where $M = Cr, Mo, W, Mn, Re$ or Os , $R = C_6H_4Me-4, C_6H_4Me-2, C_6H_4OMe-2, C_6H_4NMe_2-4$ or $C_6H_3Me_2-6$ and $L = \eta^5 - C_5H_5, \eta^5 - C_5Me_5, \eta^5 - C_9H_7 = INDENYL$, or $HB (PZ)_3 = [hydrotris (Pyrazol-1-yl) borate]$ readily add low-valent metal fragments to form stable complexes in which alkylidene groups span linkages between dissimilar transition elements. A large variety of dinuclear and polynuclear metal complexes have already been prepared by employing alkylidynes as reagents [1-6].



Alkylidynes of group VI B with iron carbonyl reagent have yielded several di and tri-metal compounds [7-8]. Treatment of $[M(\equiv CR)(OC)_2 L]$, $M = Cr, Mo$ or W and $L = \eta - C_5H_5$, $R = C_6H_3Me_2-2,6$, $M=Mo$, $L = \eta - C_5H_5$, $R = C_6H_4OMe -2$, $M = W$, $L = \eta - C_5H_5$ or C_5Me_5 or $HB (PZ)_3$, $R = C_6H_4 Me - 4$, with excess of $[Fe_2(CO)_9]$ yielded the electronically unsaturated (32 valence electron) dimetal compounds [9-11] $[M Fe (\mu - CR) (CO)_5 L]$ which reacted with elemental sulphur or selenium to produce complexes in which $\mu - \eta^2 - ECR$ groups span bonds between iron and chromium, molybdenum or tungstan, the reactions of alkylidenes $[MFe (\mu - CC_6H_3Me_2 - 2,6) (CO)_5 (\eta - C_5H_5)]$ where $M = Cr, Mo$ or W with elemental sulphur or selenium afforded compounds of the type $[M Fe (\mu - \eta^2 - E CC_6H_3 Me_2 - 2,6) (CO)_5 (\eta - C_5H_5)]$ in high yield [12].



Similarly, reactions between sulphur and alkylidenes $[MFe(\mu-C_6H_4Me-4)(CO)_5 L]$, $M = Mo$, $L = \eta-C_5H_5$ or $HB(PZ)_3$ and $M = W$, $L = \eta-C_5Me_5$, gave complexes $[MoFe(\mu-\eta^2-SCC_6H_4Me-4)(CO)_5(\eta-C_5H_5 \text{ or } \eta-HB(PZ)_3)]$ and $[WFe(\mu-\eta^2-SCC_6H_4Me-4)(CO)_5(\eta-C_5Me_5)]$ respectively. Safe introduction of sulphur and selenium in alkylidenes encouraged the authors to study reaction between tellurium and alkylidenes. Hermann and Ziegler's work [13] involving reaction of tellurium with chromium, molybdenum or tungsten complexes and Compton [14] remarks, regarding the scarcity of compounds involving the heavier main-group elements and early transition metals complexes with tellurium prompted the work described herein.

Results and Discussion

A number of compounds containing carbon to-metal triple bonds $[L(CO)_2 M(\equiv CR)]$ readily add low-valent metal fragments to form stable complexes in which alkylidene groups span linkage between dissimilar transition and non-transition elements. Using this synthetic methodology, we have earlier shown that $[M(\equiv CR)(CO)_2(\eta-C_5H_5)]$ ($M = W, Mo, Cr$, $R = C_6H_4Me-4$, C_6H_4OMe-4 , $C_6H_4NMe_2-4$, $C_6H_3Me_2-2,6$) react with $[Fe_2(CO)_9]$ to give dimetal complex $[MFe(\mu-CR)(CO)_5(\eta-C_5H_5)]$ which further react with sulphur and selenium to give $[MFe(\mu-\eta^2-SCR)(CO)_5(\eta-C_5H_5)]$ and $[MFe(\mu-\eta^2-SeCR)(CO)_5(\eta-C_5H_5)]$ respectively, (5a) - (5f) and (1a) [12].

However, many attempts failed to synthesize the analogous compounds of tellurium in the beginning. The present strategy of synthesis of compounds containing tellurium evolved after keen observations of a series of experiments where it was observed that the reactions between selenium and $[MFe(\mu-CR)(CO)_5(\eta-C_5H_5)]$ required more

vigorous conditions and time than those involving sulphur. Consequently, introduction of tellurium in $[MFe(\mu-CR)(CO)_5(\eta-C_5H_5)]$ demands more drastic environments than that of selenium. A low power ultrasonic bath was used to synthesize new compounds from reactions between tellurium and the unsaturated 32 valence electron species $[MFe(\mu-CR)(CO)_5(\eta-C_5H_5)]$ ($M = Cr, Mo, W$, $R = C_6H_3Me_2-2,6$ and $M = Mo$, $R = C_6H_4Me-4$) in Et_2O at room temperature. Use of the ultrasonic bath significantly decreased the time required for the completion of reactions and complexes $[MFe(\mu-\eta^2-TeCC_6H_3Me_2-2,6)(CO)_5(\eta-C_5H_5)]$, $M = Cr, Mo, W$ and $[MoFe(\mu-\eta^2-TeCC_6H_4Me-4)(CO)_5(\eta-C_5H_5)]$ were afforded respectively in reasonable yield. The products are similar to the previously obtained (5a), (5b), (5c), (5d), (5e), (5f) and (1a). It is noteworthy that the IR spectra of the compounds (Table-1) in the carbonyl stretching region are very similar to those of (5a) - (5f) and (1a) thus band recorded in Table-1 to be compared with heterobimetallic thio and seleno-acyl complexes [12] which serve as a model for species of this class.

The 1H and ^{13}C - $[^1H]$ NMR spectra of the compounds show the expected signal (Table-2) for these formulations. The data are very similar to those reported for compounds (5a) - (5f) and (1a) whose structures [12] were established by spectroscopic evidence and X-ray diffractions.

Experimental

All experiments were carried out under nitrogen using Schlenk tube techniques. Solvents were rigorously dried before use. Light petrol refers to that fraction of b.p. 40-60°C. Tellurium powder of particle size < 74 μm , 99.98% from E. Merck was used. IR spectra were measured with Nicolet MX10 and MX5 FT spectrometers. The compounds $[M(CC_6H_3Me_2-2,6)(CO)_2(\eta-C_5H_5)]$, $M = Mo, W$ or Cr and $[Mo(\eta-C_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ were prepared as described previously [9-12].

A suspension of $[W(\equiv CC_6H_3Me_2-2,6)(CO)_2(\eta-C_5H_5)]$ (0.78 g, 1.85 mmol) and $[Fe_2(CO)_9]$ (1.42 g, 3.9 mmol) in Et_2O (75 cm^3) was stirred overnight. The solvent and resultant $Fe(CO)_5$ were removed in vacuo. The residue was

Table-1: Analytical and physical data for the complexes

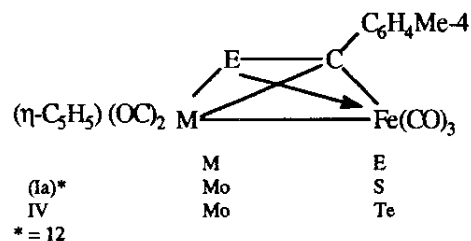
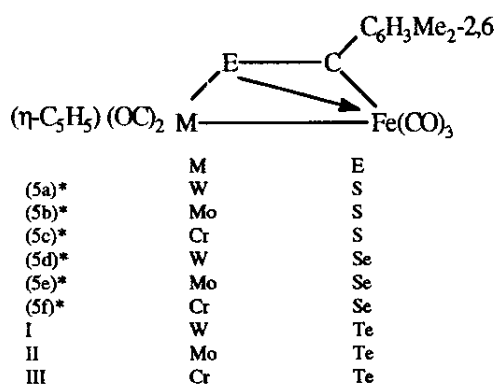
No.	Compound	Colour	Yield (%)		$\nu(\text{CO})^a$ (cm^{-1})			Analysis ^b (%)	
I	[W Fe(μ - η^2 -TeCC ₆ H ₃ Me ₂ -2,6)(CO) ₅ (η -C ₃ H ₅)]	Brown	32.97	2047 vs	1989vs	1968s	1901(bs)	(33.04)	(2.02)
II	[Mo Fe(μ - η^2 -TeCC ₆ H ₃ Me ₂ -2,6)(CO) ₅ (η -C ₃ H ₅)]	Dark brown	32.13	2045vs	1984vs	1967s	1902 (bs)	(37.87)	(2.32)
III	[Cr Fe(μ - η^2 -TeCC ₆ H ₃ Me ₂ -2,6)(CO) ₅ (η -C ₃ H ₅)]	Olive green	37.0	2049 vs	1986vs	1972s	1898 (bs)	(40.86)	(2.47)
IV	[Mo Fe(μ - η^2 -TeCC ₆ H ₄ Me-4)(CO) ₅ (η -C ₃ H ₅)]	Dark brown	43.9	2050.5 vs	1989.7 vs		1901(bs)	(36.78)	(2.04)
								36.73	2.00

a) in CH₂ Cl₂

b) Calculated values are given in parentheses.

Table-2: Hydrogen - 1 and carbon- 13NMR data for the complexes

Compound	¹ H(δ)	¹³ C(δ) ^b
I	2.40, 2.46 (sx2, 3Hx2, Me ₂ -2,6), 5.18 (s, 5H, C ₃ H ₅), 6.97-7.0 (m, 3H, C ₆ H ₃)	215.5, 214.8 (WCO), 210.6 (FeCO), 149.2 [C ¹ (C ₆ H ₃)], 136.3, 132.3 129.8, 129.2, 125.0 (C ₆ H ₃), 126.4 (CTe), 89.8 (C ₃ H ₅), 26.6, 23.8 (Me ₂ -2,6)
II	2.41, 2.50 (sx2, 3Hx2, Me ₂ -2,6) 5.10 (s, 5H, C ₃ H ₅), 6.95-7.03 (m, 3H, C ₆ H ₃)	231.1, 227.9 (MoCO), 210.4 (FeCO), 149.8 [C ¹ (C ₆ H ₃)], 136.1, 131.9, 129.4 129.0, 125.4 (C ₆ H ₃), 126.2 (CTe), 92.1 (C ₆ H ₃), 25.4, 22.8 (Me ₂ -2,6)
III	2.24, 2.32 (sx2, 3H x 2, Me ₂ -2,6), 6.5 (s, 5H, C ₃ H ₅), 6.97-7.03 (m, 3H, C ₆ H ₃)	243.1, 238.3 (CrCO), 208.7 (FeCO), 141.8 [C ¹ (C ₆ H ₃)], 140.2, 130.9, 129.3, 129.0, 126.3 (C ₆ H ₃), 112.7 (CTe), 90.8 (C ₃ H ₅), 25.8, 22.1 (Me ₂ -2,6)
IV	2.32 (s, 3H, Me-4), 5.53 (s, 5H, C ₃ H ₅) 6.43 - 7.15 (m, 4H, C ₆ H ₄)	227.5, 223.2 (MoCO), 210.5 (FeCO), 144.6 [C ¹ (C ₆ H ₄)], 138.0, 129.9, 128.5, 124.6 (C ₆ H ₄), 127.3 (CTe), 92.1 (C ₃ H ₅), 20.6 (Me - 4).

a) Chemical shifts (δ) in ppm, coupling constants in Hz, measurements at ambient temperature in CD₂Cl₂.b) Measured in CD₂Cl₂c) Hydrogen-1 decoupled, chemical shifts are positive to high frequency of SiMe₄.

treated with tellurium (0.49 g, 1.85 m mol) in Et₂O (75 cm³) and the mixture was stirred in an ultrasonic bath for 15 hours. The solvent was removed in vacuo. The residue was extracted with a mixture of CH₂ Cl₂ (6 cm³) and light petrol (14 cm³). The extract was chromatographed on a water-cooled Kieselgel Column (3x30 cm), eluting with the same solvent mixture. Initial elute containing iron carbonyl was discarded. The second fraction was collected, reduced in volume to 4cm³ in vacuo and cooled to -78°C (dry ice) to afford brown microcrystals of [W Fe(μ - η^2 - Te CC₆H₃Me₂ - 2,6)(CO)₅(η - C₃H₅)] (0.421 g).

A mixture of [Mo (\equiv CC₆H₃Me₂ - 2,6)(CO)₂(η - C₃H₅)] (0.5 g, 1.497 m mol) and [Fe₂(CO)₉] (1.16g, 3.19 m mol) was stirred in Et₂O (75 cm³) for four hours. The solvent and volatile materials were evaporated in vacuo and the residue was treated with tellurium powder (0.300 g, 2.36 m mol) in Et₂O (100 cm³) in an ultrasonic bath. The

reaction mixture was stirred overnight and the solvent was removed in vacuo. The residue was extracted with CH_2Cl_2 - light petrol (10 cm^3 , 3:7) and chromatographed on a Kieselgel 60 column ($3 \times 30\text{ cm}$). Elution with the same solvent gave a brown eluant whose volume was reduced in vacuo to get microcrystals of $[\text{Mo Fe}(\mu - \eta^2 - \text{TeCC}_6\text{H}_3\text{Me}_2-2,6)(\text{CO})_5(\eta - \text{C}_5\text{H}_5)]$ (0.617 g).

A mixture of $[\text{Cr}(\equiv\text{CC}_6\text{H}_3\text{Me}_2-2,6)(\text{CO})_2(\eta - \text{C}_5\text{H}_5)]$ (0.290 g, 1 m mol) and $[\text{Fe}_2(\text{CO})_9]$ (0.728 g, 2m mol) were stirred in Et_2O (75 cm^3) for 22 hours. The solvent along with volatile materials was removed in vacuo and the residue was treated with tellurium powder (0.200 g, 1.57 m mol) in Et_2O (75 cm^3). The reaction mixture was stirred overnight in an ultrasonic bath. The solvent was removed in vacuo and the residue was extracted in CH_2Cl_2 - light petrol mixture (10 cm^3 , 3:7). The extract was chromatographed on a water-cooled Kieselgel 60 column ($3 \times 40\text{ cm}$) with the same solvent mixture. The volume of the solvent was reduced to 4 cm^3 in vacuo and it was placed in dry ice (-78°C) where olive green microcrystals of $[\text{CrFe}(\mu - \eta^2 - \text{TeCC}_6\text{H}_3\text{Me}_2-2,6)(\text{CO})_5(\eta - \text{C}_5\text{H}_5)]$ (0.187 g) appeared.

The compound $[\text{Mo}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta - \text{C}_5\text{H}_5)]$ (0.292 g, 1 m mol) was stirred with $[\text{Fe}_2(\text{CO})_9]$ (0.768 g, 2.1 m mol) in Et_2O (75 cm^3) for 4 hours. The solvent along with volatile materials was removed in vacuo. The residue was dissolved in Et_2O (100 cm^3) and stirred with tellurium powder (0.200 g, 1.57 m mol) in an ultrasonic bath for 28 hours. The solvent was stripped off in vacuo. The residue was extracted in a mixture of CH_2Cl_2 and light petrol (10 cm^3 , 3:7) and chromatographed on a water-cooled Kieselgel Column ($3 \times 40\text{ cm}$) with the same solvent mixture. Removal of solvent in vacuo and cooling in dry ice (-78°C) afforded dark brown microcrystals of $[\text{Mo Fe}(\mu - \eta^2 - \text{TeCC}_6\text{H}_4\text{Me-4})(\text{CO})_5(\eta - \text{C}_5\text{H}_5)]$ (0.258 g).

References

1. F.G.A. Stone, Inorganic Chemistry toward the 21st century, ACS symposium No. 211, *Am. Chem. Soc.*, (1983).
2. F.G.A. Stone, Advances in organometallic chemistry, Academic Press, Inc. London, **31**, 54 (1990).
3. S.J. Dosselt, A.F. Hill, J. C. Jeffery, F. Marken, P. Sherwood and F.G.A. Stone, *J. Chem. Soc., Dalton Trans*, 2453 (1988).
4. D. Miguel, U. Steffan and F.G.A. Stone, *Polyhedron* **7**, 443 (1988).
5. A.F. Hill, F. Marken, B.A. Nasir and F.G.A. Stone, *J. Organometallic Chemistry*, **363**, 311 (1989).
6. S.J. Dosselt, A.F. Hill, J.A.K. Howard, B.A. Nasir, T.P. Spanial, P. Sherwood and F.G.A. Stone, *J. Chem. Soc., Dalton Trans*, 1871 (1989).
7. M.E. Garcia, J.C. Jeffery, P. Sherwood and F.G.A. Stone, *J. Chem. Soc., Dalton Trans*, 1209 (1987).
8. F.G.A. Stone, *J. Organometallic Chem.*, **363**, 311 (1989).
9. E. Delgado, A.T. Emo, J.C. Jeffery, N.D. Simmons and F.G.A. Stone, *J. Chem. Soc., Dalton Trans*, 1323 (1985).
10. M.E. Gracia, N.H. Tran-Hery, J.C. Jeffery, P. Sherwood and F.G.A. Stone, *J. Chem. Soc., Dalton Trans*, 2201 (1985).
11. P.G. Byren, M.E. Gracia, J.C. Jeffery, P. Sherwood and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, 12155 (1987).
12. A.F. Hill, B.A. Nasir and F.G.A. Stone, *Polyhedron*, **8**, (2) 179 (1989).
13. W.A. Hermann, C. Hechi, M.I. Ziegler and B. Balback, *J. Chem. Soc., Commun.*, 686 (1984).
14. N.A. Compton, R. Jerrington and N.C. Norman, Advances in *Organometallic Chem.* **31**, 155 (1990).