Journal of Organometallic Chemistry, 141 (1977) C21—C22
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Preliminary communication

THE SYNTHESIS OF PENTACARBONYLBIS(PHENYLTHIO)CARBENE COMPLEXES OF CHROMIUM(0) AND TUNGSTEN(0) BY THE TRAPPING OF A FREE CARBENE

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(Received September 16th, 1977)

Summary

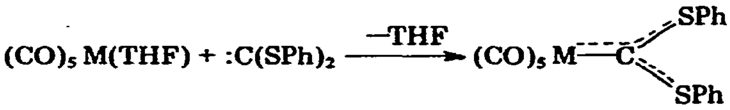
Stable dithiocarbene complexes $(CO)_5MC(SPh)_2$ (M = Cr, W) can be prepared from $(CO)_5M(THF)$ and $LiC(SPh)_3$.

Although cationic dithiocarbene complexes of osmium [1] and platinum [2] have been reported, open-chain dithiocarbene compounds of Group VI metals were hitherto unknown. Efforts to prepare such complexes of chromium from the electron-rich olefin $C_2(SMe)_4$, resulted in the metallocycle $(CO)_4\overline{CrS(Me)C(SMe)C}(SMe)S(Me)$ [3]. We have now succeeded in trapping the ligand $:C(SPh)_2$ on pentacarbonylchromium and tungsten moieties.

Seebach [4] has shown previously that the equilibrium 1 is established in

$$LiC(SPh)_3 \rightleftharpoons LiSPh + :C(SPh)_2 \qquad (1)$$

THF solution at low temperatures when $CH(SPh)_3$ is treated with BuLi. Consequently, by adding an excess of the complex $(CO)_5M(THF)$ (M = Cr, W) to a solution of $LiC(SPh)_3$ in THF, orange-red air-stable crystals of I and II in relatively low yields (not optimized) can be isolated (eq. 2). Both complexes which are soluble in a variety of organic solvents, were characterized by elemental analysis and from IR (hexane, cm^{-1}), ^1H NMR ($CDCl_3$, rel. TMS) and mass spectroscopic data.



$$(CO)_5M(THF) + :C(SPh)_2 \xrightarrow{-THF} (CO)_5M\text{---}C(SPh)_2 \qquad (2)$$

(I) M = Cr
(II) M = W

I: ν(CO), 2071s, 1981w, 1949vs; $\tau(SC_6H_5)$, 2.56s ppm; *m/e* values for molecular ion and stepwise loss of four carbonyl groups shown in mass spectrum.

II: ν(CO), 2070s, 1978w, 1945vs; $\tau(SC_6H_5)$, 2.55s ppm; *m/e* values for molecular ion and subsequent loss of five carbonyl ligands shown in mass spectrum.

Experimental

All solvents were carefully dried, deoxygenated and N_2 saturated before use. The following general method was used for the preparation of both complexes: A solution of 10 mmol BuLi in hexane was added dropwise to 10 mmol $HC(SPh)_3$ [5] in 20 ml THF at —75°C. After 20 min this yellow solution was added to a cooled (—75°C) solution of the $(CO)_5M(THF)$ complex generated photochemically (2 h) from 20 mmol $(CO)_6M$ in THF (150 ml). After stirring for 30 min at this temperature, the temperature was increased to room temperature over a period of 30 min and the solvent removed in vacuo. The desired product was extracted from the viscous residue with hexane (50 ml), the mixture concentrated to ca. 10 ml and transferred to a silica gel column. Elution of the red zone with hexane (room temperature) and recrystallization from pentane (—30°C), yielded needle-like crystals.

I: 0.08 g (0.2 mmol, 2.0% based on $HC(SPh)_3$), dec. p. 132°C. (Found: C, 51.45; H, 2.48; Cr, 12.00; S, 14.96; Mol. wt. 422 (mass spec.). $C_{18}H_{10}CrO_5S_2$ calcd.: C, 51.18, H, 2.39; Cr, 12.32; S, 15.18%; Mol. wt. 422.40.)

II: 0.11 g (0.19 mmol, 1.9% based on $HC(SPh)_3$), dec. p. 169°C. (Found: C, 39.21; H, 2.06; S, 11.31; Mol. wt. 554 (mass spec.). $C_{18}H_{10}WO_5S_2$ calcd.: C, 39.01; H, 1.82; S, 11.57%; Mol. wt. 554.25.)

Acknowledgement

We thank the Council for Scientific and Industrial Research for support of this work.

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