

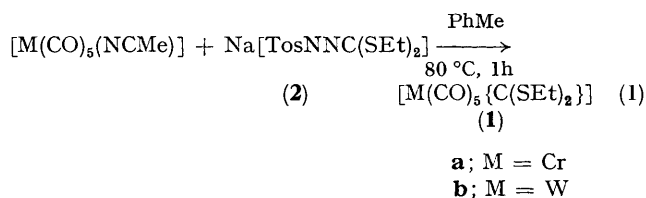
Aspects of the Co-ordination Chemistry of some Electron-rich Polyorganosulphur Compounds; Bis(ethylthio)carbene Complexes $[M(CO)_5\{C(SET)_2\}]$ ($M = Cr$ or W) from $Na[TosNNC(SET)_2]$ ($Tos = MeC_6H_4-p-SO_2$)[†]

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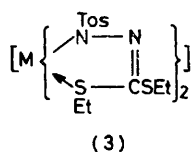
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Summary Reaction of $[M(CO)_5(NCMe)]$ ($M = Cr$ or W) with $Na[TosNNC(SET)_2]$ ($Tos = MeC_6H_4-p-SO_2$) gives the stable di(alkylthio)carbene- Cr^0 or $-W^0$ complex (see title), not formed *via* the olefin $C_2(SET)_4$, because the latter instead affords the S -, SS' -, or $SS'S''$ -olefin complex $[Cr(CO)_5(\text{olefin})]$, $[W(CO)_4(\text{olefin})]$, or $[W(CO)_3(\text{olefin})]$; d^8 metal chloro-complexes and $Na[TosNNC(SET)_2]$ yield metalocycles, such as (3).

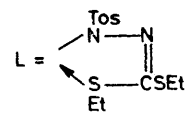
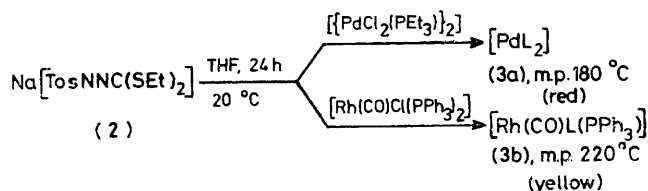
We report a new synthesis [equation (1)] of carbene-group 6-metal(0) complexes (1), using the sodium salt of the tosylhydrazone of a dithiocarbonate, (2), as carbenoid precursor.



The di(alkylthio)carbene-metal derivatives (1) (see Table) are members of a new class of carbene-ligand complex $[C(SPh)_2]$ analogues have been obtained¹ from $LiC(SPh)_3$;



they are remarkably stable, although attempts to obtain the molybdenum compound by a similar procedure were unsuccessful. The i.r. $\nu(CO)$ data for complexes (1) are appropriate for a pentacarbonyl of C_{4v} symmetry. The value of the $a_1 \nu(CO)$ mode for complex (1b) is intermediate between those for $[W(CO)_5\{C(SR)R'\}]$ and $[W\{C(NHR)R'\}-(CO)_5]$,² suggesting a charge transfer sequence from carbene ligand to $[W(CO)_5]:C(SR)R' < C(SR)_2 < C(NHR)R'$. The C_{carb} ^{13}C n.m.r. chemical shift in $[W(CO)_5\{C(SET)_2\}]$, 209 p.p.m. downfield from $SiMe_4$, is similar to that found in $[W\{CN(R)CH_2CH_2NR\}(CO)_5]$,³ but at much higher field than that for $[W(CO)_5\{C(OMe)R\}]$,² reflecting the substantial shielding of C_{carb} by π -electron donation from the adjacent S atoms.



SCHEME 1

Reaction of (2) with a d^8 metal chloro-complex affords a metalocycle (3), $[ML_2]$, (satisfactory analytical data) (*e.g.*, as

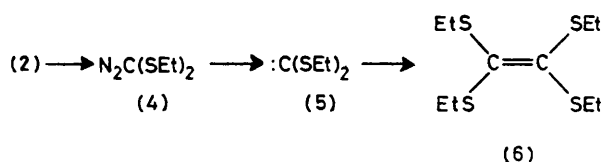
[†] No reprints available.

TABLE. Selected physical properties of some carbonylmetal(0) complexes derived from $\text{Na}[\text{TosNNC}(\text{SEt})_2]$, $\text{C}_2(\text{SEt})_4$, or $(=\text{CSCH}_2\text{CH}_2\text{S})_2$; all gave satisfactory analytical results

Compound	M.p. (°C)	Colour	I.r. $\nu(\text{CO})$ (cm^{-1}) ^a	¹ H N.m.r. ^b (τ)
(1a)	52	Orange-red	2068, 1949	6.5 q, 8.4 t
(1b)	44	Red	2066, 1942	6.4 q, 8.4 t
(7)	52–55	Yellow	2066, 1947, 1941, 1929	6.9 m, 8.5 m
(8)	38–40	Yellow-green	2025, 1920, 1902, 1894	6.85 m, 7.45 q, 8.65 t, 8.8 t
(9)	94–98	Yellow (pale)	2073, 1952, 1945, 1933	6.4 d
(10)	220 (decomp.)	Red	1994, 1927, 1900	7.0 m, 8.6 m

^a In $n\text{-C}_6\text{H}_{14}$. ^b In CDCl_3 .

in Scheme 1), in which the integrity of the N_2CS_2 skeleton is retained in the chelate ligand L. Evidently, elimination of NaCl is preferred over loss of NaTos .



SCHEME 2

The mechanism of formation of the carbenemetal complexes (1) may in principle involve three possible intermediates: the diazoalkane (4), the carbene (5), or the olefin (6) (Scheme 2), because it has been demonstrated⁴ that the tosylhydrazone salt (2) decomposes in tetrahydrofuran (THF) at 65 °C to give the olefin (6); the use of various traps makes the participation of the carbene (5) in the reaction (Scheme 2) plausible [*e.g.*,⁴ (2) + $\text{PPh}_3 \rightarrow \text{Ph}_3\text{P}=\text{C}(\text{SEt})_2$].

The olefin (6) is not implicated in the formation of the carbenemetal complexes (1), because $\text{C}_2(\text{SEt})_4$ reacts with $[\text{M}(\text{CO})_5(\text{NCMe})]$ or $[\text{M}(\text{CO})_6]$ under irradiation, using the conditions of equation (1), to give complexes $[\text{Cr}(\text{CO})_5\{\text{C}_2(\text{SEt})_4\}]$ (7) or $[\text{W}(\text{CO})_4\{\text{C}_2(\text{SEt})_4\}]$ (8); from spectroscopic data both (7) and (8) (see Table) are believed to have the metal in an octahedral environment with the olefin behaving, respectively, as an *S*- or an *SS'*-ligating donor. Similarly, $[\text{Cr}(\text{CO})_6]$ and the cyclic olefin $(=\text{CSCH}_2\text{CH}_2\text{S})_2$ gave $[\text{Cr}(\text{CO})_5(\text{olefin})]$ (9) (see Table). It is interesting to contrast these results with those on the electron-rich enamines

$\text{C}_2(\text{NMe}_2)_4$ or the cyclic $[\text{=CN}(\text{R})\text{CH}_2\text{CH}_2\text{NR}]_2$; both afford *NN'*-olefin complexes, but only the latter yields carbenemetal complexes, *e.g.*, $[\text{W}\{\text{CN}(\text{R})\text{CH}_2\text{CH}_2\text{NR}\}(\text{CO})_5]$.³ From $[\text{W}(\text{CO})_3(\text{cycloheptatriene})]$ and $\text{C}_2(\text{SEt})_4$ in *n*-hexane at 60 °C, the *SS'S'*-olefin complex $[\text{W}(\text{CO})_3\{\text{C}_2(\text{SEt})_4\}]$ (10) (see Table) was isolated.

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² *Cf.*, D. J. Cardin, B. Çetinkaya, and M. F. Lappert, *Chem. Rev.*, 1972, **72**, 545.

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⁴ U. Schöllkopf and E. Wiskott, *Angew. Chem. Internat. Edn.*, 1963, **2**, 485; D. M. Lemal and E. H. Banitt, *Tetrahedron Letters*, 1964, 245.