

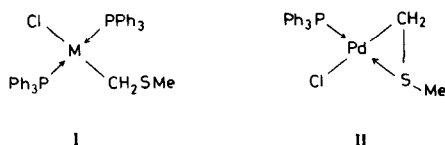
Sulphur-substituted Organometallic Compounds. Part V. Reactions of Sulphidomethyl-platinum and Palladium Compounds with Electrophilic Reagents

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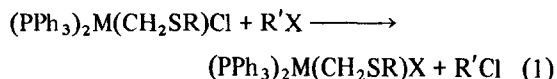
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Reports [1] have been made recently by Japanese workers on the preparation and structures of sulphidomethyl-platinum and palladium complexes, including those in which the RSCH_2 unit is acting as a monodentate ligand, e.g. in $(\text{PPh}_3)_2\text{M}(\text{CH}_2\text{SMe})\text{Cl}$ ($\text{M} = \text{Pt}$ and Pd) (I), and as a bidentate ligand, e.g. in $[(\text{PPh}_3)_2\text{MCH}_2\text{SMe}] \text{PF}_6$, $(\text{PPh}_3)\text{Pd}(\text{CH}_2\text{SMe})\text{Cl}$ (II) and $[(\text{PPh}_3)\text{Pt}(\mu\text{-CH}_2\text{SMe})\text{Cl}]_2$.



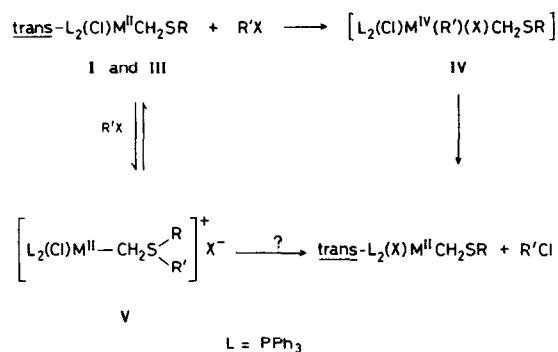
In continuation of our work [2] on sulphur containing organometallics, we have also been studying such complexes and now wish to report some reactions with electrophilic reagents. The complexes used in this work were prepared from $(\text{PPh}_3)_4\text{M}$ and ClCH_2SR ($\text{M} = \text{Pt}$ and Pd ; $\text{R} = \text{Me}$ and Ph), in essentially the same manner as that used by Okawara [1]; compounds (I) and (II) had physical properties in agreement with those published, while some data for the new $(\text{PPh}_3)_2\text{MCH}_2\text{SPh}$ compounds (III) are: $(\text{PPh}_3)_2\text{Pt}(\text{CH}_2\text{SPh})\text{Cl}$: m.p. 224–227 °C; δCH_2 1.87 (t), J_{PtH} 82 Hz, J_{PH} 8 Hz; $\nu(\text{Pt}-\text{Cl})$ 284 cm^{-1} . $(\text{PPh}_3)_2\text{Pd}(\text{CH}_2\text{SPh})\text{Cl}$: m.p. 180–183 °C; δCH_2 2.42 (s); $\nu(\text{Pd}-\text{Cl})$ 285 cm^{-1} .

Reactions of (I) and (II) ($\text{M} = \text{Pt}$ and Pd) with equivalent amounts of alkyl halides ($\text{R}'\text{X} = \text{MeI}$ and EtBr) were carried out in CHCl_3 solutions at room temperature; products were $\text{R}'\text{Cl}$ and $(\text{PPh}_3)_2\text{M}(\text{CH}_2\text{SR})\text{X}$. Evidence for formation of MeCl was found immediately on addition of MeI



to (I) or (II) and the exchanges were complete within short times. The EtBr reactions as expected were considerably slower. Other reactivity comparisons were that (i) the Pd compounds were more reactive than the Pt analogues towards MeI and (ii) the nature of R

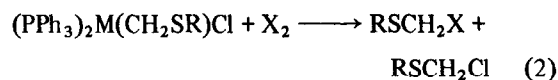
had no influence on the rate. In no case were products obtained from cleavage of the $\text{M}-\text{CH}_2\text{SR}$ bond by either MeI or EtBr . The usual mechanism for substitution reactions, involving electrophiles and Pt^{II} and Pd^{II} complexes is oxidative addition to M^{IV} complexes (e.g. IV), followed by reductive elimination. Such a mechanism can also operate for the



sulphidomethyl reactions; however complications could arise from complexation of the sulphur atom by the electrophile to give species such as (V). The species (V), and also the oxidative adducts, were undetected by n.m.r. but as low concentration intermediates, (V), could lead on to the exchange products or they could simply act as cul-de-sacs in the reaction scheme. The presence of (V) in the reaction scheme has support from Okawara's finding that MeOSO_2F and (I, $\text{M} = \text{Pt}$) provided the isolatable complex, $[(\text{Cl})(\text{PPh}_3)_2\text{PtCH}_2\text{SMe}_2]^+\text{SO}_3\text{F}^-$. Furthermore we have found that addition of $\text{CF}_3\text{CO}_2\text{H}$ to CHCl_3 solutions of (I) and (II) ($\text{M} = \text{Pd}$) at room temperature results in initial ^1H n.m.r. spectral changes (e.g. δCH_2 for III, $\text{M} = \text{Pd}$ shifts from 2.42 to 3.28) which can be attributed to protonation of

the sulphides to give $[(\text{PPh}_3)_2\text{PdCH}_2\text{SPh}]^+\text{CF}_3\text{CO}_2^-$. In contrast to the rapid reaction of (I) with MeI , the reaction of (II), containing bidentate CH_2SMe was much more sluggish. This does point to an active role for the sulphur atom of (I) and (III) in the alkyl halide reactions.

Reactions with halogens were also studied in CHCl_3 solution (Table I and equation 2). Co-ordination of the halogen to sulphides is known to generally occur [2], but



*Subsequent reaction leads to formation of MeSPh .

TABLE I. Products of Reaction of Halogens, X_2 , with $(PPh_3)_2MCl(CH_2SR)$ in $CHCl_3$ Solution at Room Temperature.

Compound	X_2	Sulphur Products
(I), M = Pd	Br_2	MeSCH ₂ Cl (20%) and MeSCH ₂ Br (80%)
(III), M = Pd	Br_2	PhSCH ₂ Cl (100%)
(III), M = Pd	I_2	PhSCH ₂ Cl (60%) and PhSCH ₂ Br (40%)
(I), M = Pt	Br_2	MeSCH ₂ Cl (20%) and MeSCH ₂ Br (80%)

such co-ordination, particularly by iodine, is not considered to play any significant role in reaction (2). To account for the products, the various isomers of the octahedral oxidative adduct, $[M(PPh_3)_2Cl(CH_2SR)(X)_2]$ (VI), have to be considered. For concerted reductive elimination of RSCH₂X or RSCH₂Cl from (VI) the relevant groups have to be in a *cis* arrange-

ment. The proportions of the products will depend thus on the relative amounts of the isomers, having RSCH₂ and a halide in the necessary *cis*-arrangement, and the relative ease of cleavage of M-halide bonds [$M-Cl > M-Br > M-I$]. The organometallic products were the appropriate diphosphinedihalide compounds.

References

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