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Preliminary communication

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ortho-METALLATION OF A SULPHUR-DONOR LIGAND: PREPARATION AND STRUCTURE OF $C_6H_4CH_2SMeMn(CO)_3(PPh_3)$

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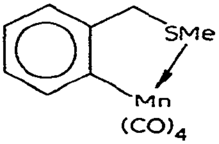
Summary

ortho-Metallation of $PhCH_2SMe$ in a reaction with $MeMn(CO)_5$ has been confirmed by a single crystal X-ray structural determination of the title complex.

Although the *ortho*-metallation reaction is now well-documented for ligands containing Group VB elements as donor atoms [1], no wel substantiated mononuclear complex containing a Group VIB element has been reported hitherto. Thus, reactions between $PdCl_2$ or $[PdCl_4]^{2-}$ and $PhCH_2SR$ (R = Me [2] or Ph [3]) have given only the complexes $PdCl_2(PhCH_2SR)_2$. Alper [4] has reported binuclear iron carbonyl complexes obtained from sulphur-donor ligands such as thiobenzophenone, some of which are considered to contain *ortho*-metallated ligands.

We report the preparation and X-ray structural identification of the first mononuclear metal complex containing a chelating *ortho*-metallated sulphur-donor ligand. The reaction between $MeMn(CO)_5$ and $PhCH_2SMe$ (refluxing heptane, 7h) affords a red non-crystallisable oil (I). [Mass spectrum: P^+ at m/e 304; other ions corresponding to $[P-n\mathrm{CO}]^+$ (n = 1—4)]. Addition



(I)

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of PPh_3 to (I), and crystallisation gave yellow $C_6H_4CH_2SMeMn(CO)_3(PPh_3)$ (II) [ν(CO): 2003vs, 1927s, 1906s cm^{-1} ; ^{1}H NMR τ 6.20s (SCH_2)*, 752s (SMe)]. A single-crystal X-ray diffraction study has confirmed the presence of the *ortho*-metallated ligand in (II).

Crystals of the title compound are triclinic, space group $P\bar{1}$, with a = 11.029(22), b = 13.485(26), c = 9.123(18) Å, α 94.52(3)°, β 109.90(3)°, γ 98.14(3)°. Observed and calculated densities are 1.42 and 1.433 g/cm^3, respectively. The structure determination was based upon 3385 nonzero independent reflections ($2\theta \leqslant 47.5°$) collected by the θ—2θ scan technique with Mo-K_α radiation on a Picker diffractometer. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares to a conventional R-factor of 0.057.

The molecular structure of $C_6H_4CH_2SMeMn(CO)_3(PPh_3)$ is shown in Fig. 1. The organosulfur ligand is bound in a chelating fashion via a Mn—S bond and a Mn—C bond to the *ortho* position of the phenyl ring. The resulting structure is of the type previously found for manganese carbonyl complexes derived from benzylideneaniline and *N,N*-dimethylbenzylamine [6]. The five-membered chelate ring is distinctly nonplanar, with the sulfur atom displaced by 0.46Å from the Mn—C(5)—C(10)—C(11) plane. Bond distances within the Mn coordination sphere are Mn—S, 2.310(4); Mn—P,

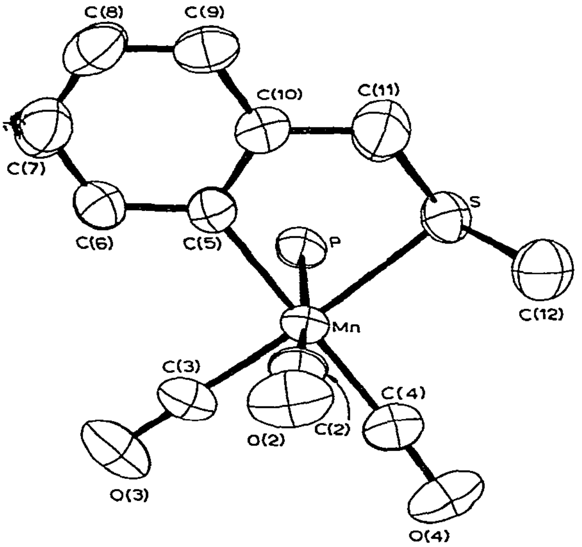

Fig.1. The molecular structure of $C_6H_4CH_2SMeMn(CO)_3(PPh_3)$. Hydrogen atoms and phenyl rings of the PPh_3 ligand are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. The atom numbering system corresponds to that used in ref. 6.

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[*] Although the CH_2 group might be expected to exhibit an AB quartet, only a slightly broadened singlet is found, even at the lowest temperature available to us (—90°). Presumably the barrier to inversion at sulphur in the five-membered ring is exceptionally low (cf. $PtCl_2(MeSCH_2CH_2SMe)$ which is resolved at room temperature [5]).

2.382(4); Mn—C(2), 1.780(6); Mn—C(3), 1.802(6); Mn—C(4), 1.799(6); Mn—C(5), 2.064(5)Å.

The two potential orientations of the *S*-methyl group with respect to the chelate ring give rise to the possibility of geometrical isomerism for (I) and (II). In fact, the methyl group in (II) lies in the less hindered site on the side of the ring opposite the PPh_3 group..

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