# Organolead Chemistry. Part 5.[1] Reactions of Bis($\eta$-cyclopentadienyl)lead(II) with Metal Halides and with Unsaturated Compounds

By **A. Kenneth Holliday, Paul H. Makin, and Richard J. Puddephatt,***† Donnan Laboratories, The University of Liverpool, Liverpool L69 3BX

Bis($\eta$-cyclopentadienyl)lead(II) acts as a Lewis base and forms a thermally stable, polymeric, complex with $BF_3$. However, with weaker Lewis acids ($BMe_3$, $BPh_3$, or $Al_2Me_6$) no adducts are formed and with many metal halides ($BCl_3$, $Al_2Cl_6$, $TiCl_3$, $VCl_3O$, or $[TaMe_3Cl_2]$) cyclopentadienyl-for-halide exchange reactions occur. The new compounds $[TaMe_3(\eta\text{-}C_5H_5)Cl]$ and a compound tentatively formulated as $[TaMe_3(\eta\text{-}C_5H_5)H]$ have been prepared in this way. The compound $Pb(\eta\text{-}C_5H_5)_2$ also gives adducts $Pb(\eta\text{-}C_5H_5)_2\cdot0.5$tcne, $Pb(\eta\text{-}C_5H_5)_2\cdot$tcne, and $Pb(\eta\text{-}C_5H_5)_2\cdot$tcnq with tetracyanoethylene (tcne) and with 7,7,8,8-tetracyanoquinodimethane (tcnq). The structures of these compounds are discussed, and the presence of tcne$^{2-}$ or tcnq$^{2-}$ is deduced.

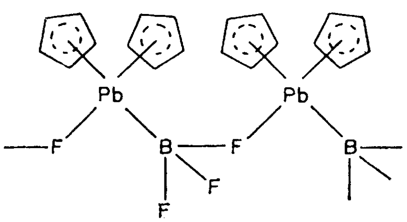
BIS($\eta$-CYCLOPENTADIENYL)LEAD(II) in the gas phase has a bent sandwich structure from which the presence of a stereochemically active lone pair of electrons on the lead atom is deduced.[2] It has been suggested that cleavage of cyclopentadienyl groups from $Pb(\eta\text{-}C_5H_5)_2$ by electrophiles occurs by initial interaction of the electrophile with this lone pair of electrons, thus giving an intermediate lead(IV) derivative which then undergoes reductive elimination [*e.g.* equation (1)].[1]

$$Pb(\eta\text{-}C_5H_5)_2 + MeI \longrightarrow [PbMe(\eta\text{-}C_5H_5)_2I] \longrightarrow Pb(\eta\text{-}C_5H_5)I + MeC_5H_5 \quad (1)$$

It can also be predicted that $Pb(\eta\text{-}C_5H_5)_2$ will have more general properties as a Lewis base as a result of the presence of the lone pair of electrons on lead. In this paper the results of a study of the donor power of $Pb(\eta\text{-}C_5H_5)_2$, by investigating its reactions with Lewis acids and with unsaturated reagents, are presented. A preliminary account of some of this work has been published.[3]

## RESULTS AND DISCUSSION

Bis($\eta$-cyclopentadienyl)lead(II), (1), on reaction with the diethyl ether–boron trifluoride (1/1) complex gave a pale yellow compound which analysed as $Pb(C_5H_5)_2(BF_3)$ (2). This compound is air-sensitive, does not melt or visibly decompose on heating to 360 °C, and is insoluble in most common organic solvents. In contrast, the analogous $Sn(C_5H_5)_2(BF_3)$ melts at 58—60 °C and is soluble in many organic solvents.[4] The great difference in physical properties between the lead and tin derivatives strongly suggests that the lead derivative is polymeric. The i.r. spectrum of (2) contained only one band in the 3 000 cm$^{-1}$ region due to the C–H stretching mode of the $C_5H_5$ groups and only one overtone band at 6 000 cm$^{-1}$. This shows that the cyclopentadienyl groups are still bound as $\eta^5$-$C_5H_5$ groups in (2).[5,6] In contrast, the indium(I) derivative $In(\eta\text{-}C_5H_5)$ apparently transforms into the $\sigma$-$C_5H_5$ bonding mode on forming the compound $In(C_5H_5)(BF_3)$.[7] The i.r. spectrum of (2) also gave bands at 1 072m, 1 048m, and 1 029m due to $\nu_{asym}$ (BF), at 782vs, 759s, and 740m due to $\nu_{sym}$ (BF), and at 521m cm$^{-1}$ due to $\delta(BF_3)$. These bands are more complex than in other $M\text{–}BF_3$ compounds and suggest asymmetry in the $BF_3$ groups.[4,7] The compound was just sufficiently soluble in [$^2H_6$]dimethyl sulphoxide to give a $^1H$ n.m.r. spectrum; this had a singlet at $\delta$ 6.00 p.p.m. with no observable coupling to $^{207}Pb$. The physical and spectroscopic properties of (2) suggest a polymeric structure (A).



(A)

In this structure each lead(II) atom can be considered to donate its lone pair of electrons to $BF_3$ and to receive a lone pair from a fluorine atom of the $BF_3$ into its vacant 6*p* orbital. Thus the stereochemistry about lead is expected to be approximately tetrahedral. It can be seen that such a structure is equivalent to a formulation $Pb(\eta\text{-}C_5H_5)_2F(BF_2)$ involving oxidative addition of a B–F bond to $Pb^{II}$, with bridging by donation of a lone pair from the Pb–F fluoride to the $BF_2$ group of a neighbouring molecule.

Compound (1) failed to give adducts with triphenylborane, trimethylborane, or trimethylaluminium and is thus a weaker Lewis base than the related $\eta$-cyclopentadienylindium(I) which forms a compound with $BMe_3$.[7] With most other metal halides, (1) did not give isolable compounds but instead cyclopentadienyl–halide exchange reactions took place. For example $TiCl_4$ gave $[Ti(\eta\text{-}C_5H_5)Cl_3]$ or $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ together with $Pb(\eta\text{-}C_5H_5)Cl$.[1] Similarly, $VCl_3O$ with (1) gave $[V(\eta\text{-}C_5H_5)_2Cl(O)]$, although in very low yield. A more interesting reaction occurred between (1) and $[TaMe_3Cl_2]$. Using a deficiency of (1), a single volatile product was formed according to equation (2).

$$Pb(\eta\text{-}C_5H_5)_2 + [TaMe_3Cl_2] \longrightarrow Pb(\eta\text{-}C_5H_5)Cl + [TaMe_3(\eta\text{-}C_5H_5)Cl] \quad (2)$$

The air-sensitive product $[TaMe_3(\eta\text{-}C_5H_5)Cl]$ could be obtained in pure form by sublimation. Subsequent to our preliminary report,[3] this compound has also been shown to be formed by reaction of $[TaMe_3Cl_2]$ with cyclopentadienylthallium(I).[8] It was characterised by elemental analysis and by the $^1H$ n.m.r. spectrum in

---

† *Present address:* Department of Chemistry, University of Western Ontario, London, Ontario, Canada.

[$^2H_8$]toluene, which contained singlets at δ 5.60 and 1.12 p.p.m. with relative intensity 5 : 9 due to the $C_5H_5$ and $Ta(CH_3)$ protons respectively. Reaction of excess of $Pb(\eta\text{-}C_5H_5)_2$ with [$TaMe_3Cl_2$] did not give the expected [$TaMe_3(\eta\text{-}C_5H_5)_2$],[8] but instead a mixture of [$TaMe_3(\eta\text{-}C_5H_5)Cl$] with a second, more volatile, and extremely air-sensitive tantalum compound was obtained. The $^1H$ n.m.r. spectrum of the product mixture in [$^2H_8$]toluene contained, as well as peaks due to [$TaMe_3(\eta\text{-}C_5H_5)Cl$], two singlets at δ 5.39 and 0.84 p.p.m. with relative intensity 5 : 9 indicating the presence of a second species [$TaMe_3(\eta\text{-}C_5H_5)X$]. Over a period of 1 week, the peaks due to this compound decayed, a precipitate was formed, and a peak due to methane appeared at δ 0.17 p.p.m. The methane was subsequently shown by mass spectrometry to contain no deuterium. The peaks due to [$TaMe_3(\eta\text{-}C_5H_5)Cl$] did not change during this period. Taking into account the known presence of [$TaMe_3(\eta\text{-}C_5H_5)Cl$], the elemental analysis of the mixture indicated that the second component had an empirical formula approximating to $TaMe_3(C_5H_5)$. Since the compound is diamagnetic it cannot be [$TaMe_3(\eta\text{-}C_5H_5)$]; a dimer [$\{TaMe_3(\eta\text{-}C_5H_5)\}_2$] would be expected to be less volatile, and the most reasonable formulation is the hydride derivative [$TaMe_3(\eta\text{-}C_5H_5)H$]. Transition-metal hydrides have been prepared previously in an analogous way and such a compound would be expected to give methane on decomposition by reductive coupling of methyl and hydride groups. However, we have been unable to identify the TaH group by $^1H$ n.m.r. or i.r. spectroscopy and the formulation must be considered tentative.

Tetracyanoethylene (tcne) with $Pb(\eta\text{-}C_5H_5)_2$ gave a bright red adduct which analysed as $Pb(C_5H_5)_2 \cdot 0.5$tcne. Using a large excess of tcne it was also possible to obtain a dark green compound $Pb(C_5H_5)_2 \cdot$tcne. Both compounds were diamagnetic and only sparingly soluble in common organic solvents. With other organometallic compounds, tcne is known to give charge-transfer complexes such as [$Fe(C_5H_5)_2$]·tcne,[9,10] salts or complexes of the radical anion tcne$^{-\cdot}$ or of the dianion tcne$^{2-}$,[11-14] or products of insertion into metal–carbon bonds.[15] The i.r. spectra in the CN stretching region have been useful in distinguishing between these formulations, and some representative data are given in the Table. The data suggest the presence of tcne$^{2-}$ in the compounds. Thus the compound $Pb(C_5H_5)_2 \cdot$tcne can be represented formally as $Pb(C_5H_5)_2{}^{2+}$tcne$^{2-}$ although undoubtedly the tcne$^{2-}$ is co-ordinated to lead, probably in a bridging mode so that the compound is polymeric. The i.r. spectrum contained only one band at 6 000 cm$^{-1}$ due to the C–H stretching overtone, and together with the observation of a singlet at δ 6.00 p.p.m. in the $^1H$ n.m.r. spectrum in [$^2H_6$]dimethyl sulphoxide solution this suggests that the cyclopentadienyl groups are still in the $\eta^5$ bonding form. This is perhaps surprising since other cyclopentadienyl-lead(IV) compounds contain σ-bonded $C_5H_5$ groups.[5] It is difficult to formulate a reasonable structure for the compound $Pb(C_5H_5)_2 \cdot$ 0.5tcne. The spectroscopic data are very similar to those for $Pb(\eta\text{-}C_5H_5)_2 \cdot$tcne, indicating the presence of tcne$^{2-}$, but the compound cannot contain [$Pb(\eta\text{-}C_5H_5)_2$]$^{+\cdot}$ and it is possible that it should be formulated as $Pb(\eta\text{-}C_5H_5)_2{}^{2+}\cdot$tcne$^{2-}\cdot Pb(\eta\text{-}C_5H_5)_2$.

Infrared spectra (cm$^{-1}$) of some derivatives of tetracyanoethylene (tcne) and 7,7,8,8-tetracyanoquinodimethane (tcnq)

| Compound [a] | $\nu$(CN) |
|---|---|
| tcne | 2 262, 2 215 |
| [$Fe(\eta\text{-}C_5H_5)_2$]·tcne | 2 255, 2 216 |
| $Na^+$tcne$^{-\cdot}$ | 2 209, 2 183 |
| $2Na^+$tcne$^{2-}$ | 2 160, 2 095 |
| [$Co(\eta\text{-}C_5H_5)_2$]$^+$tcne$^{-\cdot}$ | 2 190 |
| $Pb(\eta\text{-}C_5H_5)_2 \cdot 0.5$tcne | 2 182, 2 168, 2 082 |
| $Pb(\eta\text{-}C_5H_5)_2 \cdot$tcne | 2 178, 2 098 |
| $Pb(\eta\text{-}C_5H_5)_2 \cdot 0.5$tcne [b] | 2 198, 2 175, 2 162, 2 098 |
| tcnq | 2 200, 2 150 |
| tcnq$^{-\cdot}$ | 2 198—2 193 |
| tcnq$^{2-}$ | 2 151, 2 102 |
| $Pb(\eta\text{-}C_5H_5)_2 \cdot$tcnq | 2 184, 1 170 (sh), 2 130, 2 093 |

[a] As Nujol mulls unless otherwise stated. [b] Solution in tetrahydrofuran.

With 7,7,8,8-tetracyanoquinodimethane (tcnq), $Pb(\eta\text{-}C_5H_5)_2$ gave only a pale green, diamagnetic, 1 : 1 adduct $Pb(\eta\text{-}C_5H_5)_2 \cdot$tcnq. The CN stretching frequencies are lower than in tcnq$^{-\cdot}$ and suggest the presence of tcnq$^{2-}$.[16-18] The compound is therefore formulated as $Pb(\eta\text{-}C_5H_5)_2{}^{2+}$tcnq$^{2-}$, although its low solubility indicates tcnq$^{2-}$ bridges between lead centres giving a polymeric structure. The presence of $\eta\text{-}C_5H_5$ groups was again deduced from the presence of a single C–H stretching vibration at 3 000 cm$^{-1}$ and a single overtone at 6 000 cm$^{-1}$ in the i.r. spectrum.[5] The presence of bridging tcne and tcnq in some tin(IV) derivatives of tcne$^{-\cdot}$ and tcnq$^{-\cdot}$ has been deduced.[13]

*Conclusions*.—It is of interest to compare the properties of $Pb(\eta\text{-}C_5H_5)_2$ with those of $Sn(\eta\text{-}C_5H_5)_2$ and of $In(\eta\text{-}C_5H_5)$. It is clear that $Pb(\eta\text{-}C_5H_5)_2$ is a weaker Lewis base than is $In(\eta\text{-}C_5H_5)$ but is similar to $Sn(\eta\text{-}C_5H_5)_2$.[4,7,19] However, it is clear that cyclopentadienyl groups are cleaved from lead more readily than from tin. Thus $Sn(\eta\text{-}C_5H_4Me)_2$ forms a simple complex with aluminium(III) chloride,[19] but $Pb(\eta\text{-}C_5H_5)_2$ with this reagent undergoes cleavage of a cyclopentadienyl group to give $Pb(\eta\text{-}C_5H_5)Cl$. A similar trend may be noted with $In(\eta\text{-}C_5H_5)$ and $Tl(\eta\text{-}C_5H_5)$, where the thallium derivative undergoes cyclopentadienyl-for-halide exchange more readily.[7]

Another recognisable difference between cyclopentadienyl derivatives of $Sn^{II}$ and $Pb^{II}$ is the tendency to give polymeric complexes. Thus $Pb(\eta\text{-}C_5H_5)_2$,[20] $Pb(\eta\text{-}C_5H_5)Cl$,[1] $Pb(\eta\text{-}C_5H_5)_2(BF_3)$, and $Pb(\eta\text{-}C_5H_5)_2 \cdot$tcne are probably all polymeric in the solid state whereas analogous derivatives of $Sn^{II}$ are probably monomeric.[4,10,21] This tendency to form polymers appears to arise because lead prefers a higher co-ordination number than tin and this is achieved by ligands bridging between lead centres to give polymeric structures. Such bridging may well facilitate cyclopentadienyl-for-halide exchange reactions, which occur more readily with $Pb(\eta\text{-}C_5H_5)_2$ than for $Sn(\eta\text{-}C_5H_5)_2$.

## EXPERIMENTAL

The preparation of $Pb(\eta\text{-}C_5H_5)_2$ and general experimental methods have been described previously.[1] All the experiments with $Pb(\eta\text{-}C_5H_5)_2$ were conducted in an atmosphere of dry nitrogen or *in vacuo*,

*Reaction of Bis*($\eta$-*cyclopentadienyl*)*lead*(II).—*With boron trifluoride*. To a solution of $Pb(\eta\text{-}C_5H_5)_2$ (2.0 g, 6.0 mmol) in dry benzene (15 $cm^3$) was added $OEt_2{\cdot}BF_3$ (0.84 g, 6.0 mmol). After 1 h at room temperature, the pale yellow precipitate of $Pb(\eta\text{-}C_5H_5)_2(BF_3)$ was filtered off, washed with dry benzene, and dried *in vacuo*, yield 75%. The compound did not melt or visibly decompose on heating to 360 °C (Found: C, 29.4; H, 3.3; F, 13.8. Calc. for $C_{10}H_{10}BF_3Pb$: C, 29.8; H, 3.0; F, 14.0%).

*With triphenylborane, trimethylborane, or trimethylaluminium*. To a solution of $Pb(\eta\text{-}C_5H_5)_2$ (2.0 g, 6.0 mmol) in benzene (15 $cm^3$) was added a solution of $BPh_3$ (6.0 mmol) in benzene (20 $cm^3$). After 2 d the volume of the solution was reduced to 10 $cm^3$ *in vacuo*, and the yellow precipitate was filtered off and identified as unchanged $Pb(\eta\text{-}C_5H_5)_2$. Similarly, evaporation of solutions of $Pb(\eta\text{-}C_5H_5)_2$ with $BMe_3$ or $Al_2Me_6$ in benzene gave only unchanged $Pb(\eta\text{-}C_5H_5)_2$ as residue.

*With titanium*(IV) *chloride*. The compound $TiCl_4$ (1.13 g, 6 mmol) was added dropwise to a solution of $Pb(\eta\text{-}C_5H_5)_2$ (6 mmol) in benzene (15 $cm^3$). A dark green precipitate formed immediately but this rapidly became orange on stirring the mixture. The precipitate was filtered off and was then fractionally sublimed to give first $[Ti(\eta\text{-}C_5H_5)Cl_3]$ (m.p. 180—190 °C, 48%) and then $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ (m.p. 290 °C, 23%), identified by comparison (m.p., n.m.r. spectrum) with authentic samples. The residue was identified as impure $Pb(\eta\text{-}C_5H_5)Cl$ by comparison with an authentic sample (i.r. and mass spectra, m.p.).[1]

In a similar reaction of $TiCl_4$ (3 mmol) with $Pb(\eta\text{-}C_5H_5)_2$ (6 mmol), $[Ti(\eta\text{-}C_5H_5)_2Cl_2]$ was obtained in 50% yield with no $[Ti(\eta\text{-}C_5H_5)Cl_3]$.

*With dichlorotrimethyltantalum*(V). A solution of $[TaMe_3Cl_2]$ (6 mmol) [22] in pentane (10 $cm^3$) was added to a solution of $Pb(\eta\text{-}C_5H_5)_2$ (3 mmol) in benzene (15 $cm^3$). After 1 h, the solvent was evaporated and the residue was sublimed giving orange-yellow crystals of $[TaMe_3(\eta\text{-}C_5H_5)Cl]$, which were very sensitive to air, sublimed 65—70 °C ($10^{-3}$ Torr) * (Found: C, 29.0; H, 4.3; Cl, 10.6; Ta, 54.6. Calc. for $C_8H_{14}ClTa$: C, 29.4; H, 4.3; Cl, 10.9; Ta, 55.6%).

In other experiments using an equimolar amount or excess of $Pb(\eta\text{-}C_5H_5)_2$ the product also contained a more volatile and extremely air-sensitive yellow compound. A complete separation from $[TaMe_3(\eta\text{-}C_5H_5)Cl]$ was not possible and a typical sample gave the following analysis {Found: C, 29.6; H, 4.2; Cl, 3.4. Calc. for a $[TaMe_3(\eta\text{-}C_5H_5)Cl]$-$[TaMe_3(\eta\text{-}C_5H_5)H]$ mixture (1 : 2): C, 30.1; H, 4.6; Cl, 3.9%}. An attempt to reduce the mixture with $Na[BH_4]$ led to general decomposition.

*With trichloro-oxovanadium*(V). The compound $VCl_3O$ (1.0 g, 6 mmol) was condensed into a solution of $Pb(\eta\text{-}C_5H_5)_2$ (2 g, 6 mmol) in benzene (15 $cm^3$) cooled in liquid nitrogen. A deep blue-black precipitate formed on warming to room temperature. The solvents were evaporated and the residue was heated under high vacuum when blue crystals of $[V(\eta\text{-}C_5H_5)_2Cl(O)]$ sublimed in low yield (2%) at 170—190 °C. Attempts to improve the yield by varying the stoicheiometry and work-up procedure were unsuccessful (Found: C, 51.8; H, 4.5. Calc. for $C_{10}H_{10}ClOV$: C, 51.6; H, 4.3%). N.m.r. spectrum in $CDCl_3$: $\delta(C_5H_5)$ 6.25(s) p.p.m.

*With tetracyanoethylene*. (*a*) A solution of tetracyanoethylene (0.38 g, 3 mmol) in benzene (10 $cm^3$) was added to a solution of $Pb(\eta\text{-}C_5H_5)_2$ (2.0 g, 6 mmol) in benzene (15 $cm^3$). A bright red precipitate of $Pb(\eta\text{-}C_5H_5)_2{\cdot}0.5$tcne formed immediately. This was filtered off, washed thoroughly with benzene, and dried *in vacuo*, yield 60%. It decomposed without melting at 180 °C (Found: C, 38.7; H, 2.6; N, 7.3. Calc. for $C_{13}H_{10}N_2Pb$: C, 38.9; H, 2.5; N, 7.0%). The same product was formed when the reaction was carried out using a 1 : 1 mol ratio of reagents (Found: C, 37.1; H, 2.5%).

(*b*) A solution of $Pb(\eta\text{-}C_5H_5)_2$ (1.0 g, 3 mmol) in benzene (10 $cm^3$) was added dropwise to a solution of tcne (1.52 g, 12 mmol) in benzene (25 $cm^3$). The dark green precipitate of $Pb(\eta\text{-}C_5H_5)_2{\cdot}$tcne which formed was filtered off, washed thoroughly with benzene, and dried *in vacuo*, yield 84%. It decomposed without melting at 180 °C (Found: C, 40.6; H, 2.3; N, 10.6. Calc. for $C_{16}H_{10}N_4Pb$: C, 41.3; H, 5.15; N, 12.0%).

*With* 7,7,8,8-*tetracyanoquinodimethane* (*tcnq*). A solution of $Pb(\eta\text{-}C_5H_5)_2$ (2.0 g, 6 mmol) in benzene (15 $cm^3$) was added to a solution of tcnq (1.2 g, 6 mmol) in benzene (10 $cm^3$). The dark green precipitate of $Pb(\eta\text{-}C_5H_5)_2{\cdot}$tcnq was filtered off, washed thoroughly with benzene, and dried *in vacuo*, yield 62%. It decomposed without melting at 205 °C (Found: C, 48.9; H, 2.8; N, 10.6. Calc. for $C_{22}H_{14}N_4Pb$: C, 48.8; H, 2.6; N, 10.35%). The same product was formed using an excess of $Pb(\eta\text{-}C_5H_5)_2$.

We thank Dr. J. D. Wilkins for a gift of $[TaMe_3Cl_2]$, Dr. K. R. Seddon for $VCl_3O$, and the Associated Octel Company Ltd. for support (to P. H. M.).

[8/331 *Received, 24th February*, 1978]

## REFERENCES

[1] Part 4, A. K. Holliday, P. H. Makin, and R. J. Puddephatt, *J.C.S. Dalton*, 1976, 435.

[2] A. Almenningen, A. Haaland, and T. Motzfeldt, *J. Organometallic Chem.*, 1967, **7**, 97.

[3] A. K. Holliday, P. H. Makin, R. J. Puddephatt, and J. D. Wilkins, *J. Organometallic Chem.*, 1973, **57**, C45.

[4] P. G. Harrison and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1970, **92**, 2577.

[5] E. W. Abel, M. O. Dunster, and A. Waters, *J. Organometallic Chem.*, 1973, **49**, 287.

[6] A. Davison and P. E. Rakita, *J. Organometallic Chem.*, 1970, **23**, 407.

[7] J. G. Contreras and D. G. Tuck, *Inorg. Chem.*, 1973, **12**, 2596.

[8] R. R. Schrock, *J. Amer. Chem. Soc.*, 1975, **97**, 6577.

[9] A. Adman, M. Rosenblum, S. Sullivan, and T. N. Margulis, *J. Amer. Chem. Soc.*, 1967, **89**, 4540.

[10] J. A. Richards and P. G. Harrison, *J. Organometallic Chem.*, 1974, **64**, C3.

[11] R. L. Brandon, J. H. Osieki, and A. Ottenberg, *J. Amer. Chem. Soc.*, 1966, **31**, 1214.

[12] W. Beck, R. Schlodder, and K. H. Lechler, *J. Organometallic Chem.*, 1973, **54**, 303.

[13] A. B. Cornwell, P. G. Harrison, and J. A. Richards, *J. Organometallic Chem.*, 1974, **67**, C43; 1977, **140**, 273.

[14] P. J. Krusic, H. Stoklosa, L. E. Manzer, and P. Meakin, *J. Amer. Chem. Soc.*, 1975, **97**, 667.

[15] H. C. Gardner and J. K. Kochi, *J. Amer. Chem. Soc.*, 1976, **98**, 2460.

[16] A. R. Siedle, *J. Amer. Chem. Soc.*, 1975, **97**, 5931.

[17] S. G. Clarkson, B. C. Lane, and F. Basolo, *Inorg. Chem.*, 1972, **11**, 662.

[18] D. S. Acker and W. R. Hertler, *J. Amer. Chem. Soc.*, 1962, **84**, 3370; L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *ibid.*, p. 3374.

---

* Throughout this paper: 1 Torr = (101 325/760) Pa.

[19] J. Doe, S. Borkett, and P. G. Harrison, *J. Organometallic Chem.*, 1973, **52**, 343.

[20] G. Bombieri and C. Panattoni, *Acta Cryst.*, 1966, **20**, 595; C. Panattoni, G. Bombieri, and U. Croatto, *ibid.*, **21**, p. 823.

[21] K. D. Bos, E. J. Bulten, J. G. Noltes, and A. L. Spek, *J. Organometallic Chem.*, 1975, **99**, 71.

[22] G. W. A. Fowles, D. A. Rice, and J. D. Wilkins, *J.C.S. Dalton*, 1973, 961.