Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

REACTIONS OF HYDRIDOCARBONYLTRIS(TRIPHENYLPHOSPHINE)-RHODIUM WITH ALKYNES

B. L. BOOTH AND A. D. LLOYD

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD (Great Britain)

(Received August 2nd, 1971)

SUMMARY

The hydride, $RhH(CO)(PPh_3)_3$, reacts with the alkynes RC_2R (where $R = CO_2Me$, CO_2Et, CO_2H or C_6H_5), to give stable adducts of the type $RCH{=}CR{-}Rh(CO)(PPh_3)_2$. Cleavage of the adducts where $R = CO_2Me$ or C_6H_5 with anhydrous HCl gives dimethyl fumarate and *trans*-stilbene respectively, indicating that these adducts have a *trans*-configuration about the double bond. The similar reaction of the hydride with perfluoro-1-butyne also gives a stable, crystalline adduct, $CF_3{-}CH{=}C(CF_3){-}Rh(CO)(PPh_3)_2$, which has been shown by NMR spectroscopy to have a *cis*-configuration, implying that a different mechanism operates in this reaction.

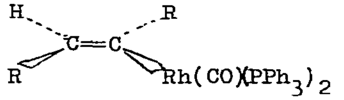
INTRODUCTION

The hydride, $RhH(CO)(PPh_3)_3$ is an efficient catalyst for homogeneous hydrogenation[1], isomerisation[2-4] and hydroformylation[2,5] of olefins. One of the key steps in each of these reactions is the insertion of an olefin into the rhodium–hydrogen bond. Recent work[6] has shown that, with the exception of an adduct from tetrafluoroethylene, the σ-alkyl complexes obtained by reaction of the hydride with alkenes are extremely labile, as expected in view of the high catalytic activity of the hydride. Whereas allene and certain conjugated dienes, which inhibit catalysis, do yield stable π-allyl complexes upon reaction with the hydride[7]. Our interest[8,9] in the stereochemistry of hydride addition reactions led us to investigate some reactions of $RhH(CO)(PPh_3)_3$ with some electron-deficient alkynes in the hope that these would yield stable complexes, and lead to a better understanding of the hydride addition step; these reactions are now reported. While this work was in progress some similar reactions of $IrH(CO)(PPh_3)_3$ with alkynes were reported[10] and brief mention was made to the fact that these authors had also investigated the reactions of the rhodium analogue, but as far as we are aware no details have been reported.

RESULTS AND DISCUSSION

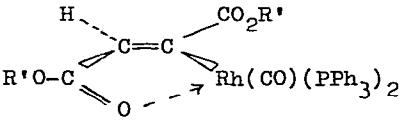
When a suspension of $RhH(CO)(PPh_3)_3$ in ether is shaken at room temperature with dimethyl acetylenedicarboxylate the yellow, crystalline solid $MeO_2C{-}CH{=}$

$C(CO_2Me)-(RhCO)(PPh_3)_2$ is obtained in 81% yield. Its IR spectrum shows a metal carbonyl band at 1965 cm^{-1}, two strong bands at 1708 and 1685 cm^{-1} attributable to the ester carbonyl groups, and a medium strong band at 1522 cm^{-1} [ν(C=C)]. The presence in the spectrum of two bands for the ester carbonyl groups and the absence[8] of any strong band in the region of 1495–1550 cm^{-1} supports a four-coordinate arrangement about the rhodium atom [structure (I)], rather than an alternative structure (II) in which one of the ester carbonyl groups also coordinates to the metal atom to give a five-coordinate species. The position of the metal–carbonyl band, which is similar to that of *trans*-$RhCl(CO)(PPh_3)_2$ [ν(CO) 1960 cm^{-1}][11], is consistent with a *trans*-square planar arrangement about the rhodium atom. When complex (I) is cleaved with dry hydrogen chloride in benzene at room temperature the only organic product isolated (in 68% yield) is dimethyl fumarate. Wilkinson *et al.*[6] have shown that the complex $CHF_2-CF_2-Rh(CO)(PPh_3)_2$ undergoes an oxidative-addition reaction with HCl to give an intermediate Rh^{III}–HCl adduct, which on warming to room temperature decomposes with hydrogen transfer to give 1,1,2,2-tetrafluoroethane. It seems very probable that cleavage of compound (I) occurs in a similar manner, and it is reasonable to assume that the hydrogen transfer to the σ-alkenyl carbon atom will occur with retention of configuration about the double bond; as previously demonstrated for the acid cleavage of certain alkenylmanganese carbonyl complexes[12,13]. On this basis it is considered that the formation of dimethyl fumarate on acid cleavage of (I) establishes a *trans*-configuration about the double bond.

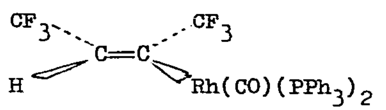


(I) R = CO_2Me; (III) R = CO_2Et

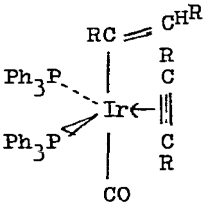
(IV) R = CO_2H; (V) R = C_6H_5



(II)



(VI)



(VII) R = CF_3 or CO_2Me

Diethyl acetylenedicarboxylate and acetylenedicarboxylic acid react similarly with $RhH(CO)(PPh_3)_3$ at room temperature to give the adducts (III) and (IV) in 25% and 72% yields respectively. The IR spectrum of compound (IV) shows, in addition to the metal carbonyl band at 1970 cm^{-1}, bands at 1690 and 1645 cm^{-1} for the carboxyl carbonyl groups, and a band at 1575 cm^{-1}. Although this last band is in the region expected[8] for a coordinated carbonyl group [structure (II)] in view of the fact that both carboxyl carbonyl groups also are apparent in the spectrum it seems more likely that compound (IV) has a four-coordinate structure and that the band at 1575 cm^{-1} is due to the C=C bond. The IR spectrum of (III) shows some significant differences from those of compounds (I) and (IV) in that only one band at 1680 cm^{-1} is apparent in the ester carbonyl region, and there is a strong band at 1565 cm^{-1} which does not appear in the spectrum of (I). This may indicate that compound (III) is five-coordinate. Some difficulty was experienced in isolating this compound, and it is possible that although a four-coordinate complex is formed as the initial reaction product some rearrangement to the five-coordinate complex may have occurred during the work-up procedure. Although acid cleavage of the compounds (III) and (IV) has not been undertaken it seems probable that these compounds also have a *trans*-configuration about the double bond.

The reaction of the hydride with diphenylacetylene gives the yellow, crystalline adduct (V) in 82% yield. This compound, which must necessarily be four-coordinate, shows a metal–carbonyl band at 1960 cm^{-1} in its IR spectrum, and a weak band at 1590 (or 1570) cm^{-1} for the C=C bond. Cleavage of this adduct with anhydrous HCl gives *trans*-stilbene as the only organic product. When this cleavage reaction was monitored by IR spectroscopy no *cis*-stilbene was detected at any stage during the reaction, and a control experiment in which *cis*-stilbene was shaken with dry HCl in benzene under identical conditions to those employed in the cleavage reaction failed to give any *trans*-stilbene. These results imply that the adduct (V) also has a *trans*-configuration. The other products isolated from this cleavage reaction were $RhCl(CO)(PPh_3)_2$ and a pale yellow crystalline solid which analysed correctly for $RhHCl_2(CO)(PPh_3)_2$. Its IR spectrum showed metal carbonyl bands at 2041 and 1953 cm^{-1}, and a rhodium–hydrogen stretching frequency band at 2105 cm^{-1}. The spectrum was similar in all respects to the previously reported compounds $RhHCl_2(CO)L_2$ (where L=$AsPh_3$ or $SbPh_3$)[14] [*cf.* where L=$AsPPh_3$, $\nu(CO)=2067$; $\nu(Rh\text{–}H)=2087$ cm^{-1}; where L=$SbPh_3$, $\nu(CO)=2062$; $\nu(Rh\text{–}H)=2035$ cm^{-1}] apart from the presence of two metal carbonyl bands, which probably indicates that the product is a mixture of stereoisomers.

The reaction between $RhH(CO)(PPh_3)_3$ and hexafluoro-2-butyne occurs readily at room temperature to afford the yellow, crystalline adduct (VI) in 83% yield. Its IR spectrum shows a metal–carbonyl band at 1985 cm^{-1}, a weak–medium band at 1604 cm^{-1} [ν(C=C)], and strong ν(C–F) bands in the region of 1090–1345 cm^{-1}. Its ^1H NMR spectrum shows a quartet (J 10.7 Hz) at τ 5.16 arising from coupling of a vinylic proton with a geminal CF_3 group, and further quartet splitting (J 2.5 Hz) arises by coupling of this proton to the *trans*-CF_3 group; the magnitude of the ^1H–^{19}F coupling to the vicinal CF_3 group is more consistent with a *trans*-H–CF_3 arrangement (*ie.* a *cis*-adduct) than a *cis*-H–CF_3 arrangement (*trans*-adduct)[15–17]. The ^{19}F NMR spectrum shows a quartet (J 11.2 Hz) at −27.1 ppm downfield from external trifluoroacetic acid for a CF_3 group geminal to the rhodium atom, and in agreement with this assignment this band is further split into doublets (J 2.5 Hz) by coupling to the *trans*-vinylic proton. The other CF_3 group appears as a quartet of doublets at −19.9 ppm due to coupling with the *cis*-vicinal CF_3 group and the geminal vinylic proton; the large ^{19}F–^{19}F coupling constant again supports[15–17] the assignment of a *cis*-configuration to this compound.

This difference in the stereochemistry of the hydride addition reaction with hexafluoro-2-butyne and the other acetylenes employed in this work could be explained in terms of *cis–trans* isomerisation of adducts formed initially in the reactions with the acetylenes RC_2R (where $R=CO_2Me$, CO_2H, CO_2Et or Ph); a similar isomerisation has been shown to occur on heating some analogous (perfluorovinyl)-arsenic compounds[16]. However, the mild conditions employed for these reactions make this explanation unlikely, and a more reasonable assumption is that the change in stereochemistry is indicative of a change in reaction mechanism. It has been previously established[18] that the initial step in the reactions of $RhH(CO)(PPh_3)_3$ and similar complexes with unsaturated ligands is dissociation of a triphenylphosphine ligand to give $RhH(CO)(PPh_3)_2$. This coordinatively unsaturated hydride is then considered to react with the unsaturated ligand, in this case an acetylene molecule, to form a five-coordinate π-complex. In the case of the acetylenes where $R=CO_2Me$, CO_2Et, CO_2H or C_6H_5 it seems probable that these π-complexes will be relatively unstable, and that the equilibrium will lie well over on the hydride side. In these cases an alternative reaction pathway involving direct attack of $RhH(CO)(PPh_3)_2$ on the acetylene, either by a free radical or nucleophilic mechanism, could operate, leading to formation of the *trans*-adducts, as previously observed for reactions between other metal carbonyl hydrides and electron-deficient acetylenes[8,19]. In the case of the reaction with hexafluoro-2-butyne the π-complex would be expected to be more stable, and may have a sufficiently long lifetime to enable *cis*-hydride transfer to occur from the rhodium atom to the acetylenic carbon atom with the formation of the isolated *cis*-adduct, *i.e.* a similar mechanism to that postulated to occur in the reaction between *cis*-$(Et_3P)_2PtHCl$ and hexafluoro-2-butyne[15,20]. In this context it would be interesting to compare the stereochemistry of addition of $RhH(CO)(PPh_3)_3$ to acetylenes with that of $IrH(CO)(PPh_3)_3$, since the π-acetylene–IrH complexes should be more stable and should give *cis*-adducts with the majority of disubstituted acetylenes. Although the reactions of the iridium hydride with acetylenes have been reported[10] and have been shown to give a rather different type of complex (VII), the stereochemistry of the addition step was not commented on. This difference in the type of complex obtained from the iridium analogue compared with those obtained in this work with the rhodium hydride is probably due to the different reaction conditions employed. The reactions with $IrH(CO)(PPh_3)_3$ were carried out using an excess of the acetylene and a reaction temperature of 70°, rather than a 1/1 acetylene/hydride ratio at room temperature as used in this work.

The complexes isolated during this work are all reasonably stable in air, and show no tendency to dissociate at room temperature in solution, unlike the fluoroalkyl complex $Rh(CF_2CF_2H)(CO)(PPh_3)_2$[6], although we have yet to investigate the properties of these compounds at higher temperatures.

EXPERIMENTAL

IR spectra were recorded on a Perkin–Elmer 621 grating instrument as mulls in Nujol and HCB, and NMR spectra were recorded on a Perkin–Elmer R10, a Varian HA100 or a Hitachi–Perkin–Elmer R20A instrument. Molecular weight determinations were carried out using a Mechrolab vapour pressure osmometer. Chromatographic separations were carried out using either deactivated alumina (Grade H) or Florisil (100–200 u.s. mesh). All solvents were dried and de-aerated before use, and light petroleum had a boiling range of 40–60°. Except where stated, all reactions were carried out under an atmosphere of dry nitrogen.

Dimethyl and diethyl acetylenedicarboxylate, acetylenedicarboxylic acid, and diphenylacetylene were commercial samples used without further purification, as were the samples of rhodium trichloride trihydrate and triphenylphosphine. Hexafluoro-2-butyne was prepared by a previously reported procedure[21]. *cis*-Stilbene was obtained in 10% yield by reduction of diphenylacetylene using a copper–zinc couple and glacial acetic acid[22]. Hydridocarbonyltris(triphenylphosphine)rhodium was prepared from rhodium trichloride trihydride using the method previously reported by Wilkinson *et al.*[18].

Reactions of hydridocarbonyltris(triphenylphosphine)rhodium

(*a*). *With dimethyl acetylenedicarboxylate.* The acetylene (0.2 g, 1.4 mmole) was added to a suspension of the hydride (1.0 g, 1.08 mmole) in diethyl ether (50 ml), and the mixture was shaken for 30 min. Filtration gave a yellow solid, which was recrystallised from acetone to give dimethyl[carbonylbis(triphenylphosphine)rhodio]fumarate (I) (0.7 g, 81%), m.p. 155° (with decomp.). [Found: C, 64.6; H, 4.8; mol.wt., 754 (benzene). $C_{43}H_{37}O_5P_2Rh$ calcd.: C, 64.7; H, 4.6%; mol.wt., 798.] Its IR spectrum showed bands at 3050 m, 2990 w, 2940 s, 2790 w, 2730 w, 1965 vs, 1730 m, 1708 s, 1685 s, 1655 m, 1605 w, 1522 m, 1475 w, 1431 vs, 1390 m, 1330 m, 1315 m, 1240 m, 1205 m, 1180 m, 1155 m, 1110 m, 1105 m, 1090 m, 1033 w, 1024 w, 1005 w, 995 w, 935 w, 890 w, 860 w, 785 w, 772 w, 750 m(sh), 740 m, 719 m, 700 m, 690 s, 572 s and 495 m cm^{-1}. Its ^1H NMR spectrum ($CDCl_3$, with TMS internal reference; 100 MHz) showed bands at τ 2.5 (30, complex multiplet: aromatic protons), 5.49 (1, singlet; vinylic proton), 6.74 (3, singlet; OCH_3 protons) and 6.98 (3, singlet; OCH_3 protons).

(*b*). *With diethyl acetylenedicarboxylate.* When the acetylene (0.5 g, 2.9 mmole) was shaken at room temperature for 3 days with a suspension of the hydride (2.0 g, 2.16 mmole) in ether (50 ml), a yellow solid (1.5 g) was obtained after filtration. Chromatographic separation on Florisil(diethylether eluant) gave yellow crystals of diethyl[carbonylbis(triphenylphosphine)rhodio]fumarate (III) (0.6 g, 25%), m.p. 145° (with decomp.); considerable decomposition occurred during chromatography, and attempts to purify the product by the alternative procedure of recrystallisation from acetone or from a mixture of dichloromethane and light petroleum were unsuccessful. (Found: C, 64.8; H, 4.5. $C_{45}H_{41}O_5P_2Rh$ calcd.: C, 65.4; H, 5.0%.) Its ^1H NMR spectrum ($CDCl_3$, 100 MHz) showed bands at τ 2.5 (30, complex multiplet; aromatic protons), 5.46 (1, singlet; vinylic proton), 6.28 (2, quartet, *J* 7 Hz; CH_2 protons), 6.40 (2, quartet, *J* 7 Hz; CH_2 protons), 9.03 (3, triplet, *J* 7 Hz; CH_3 protons) and 9.36 (3, triplet, *J* 7 Hz; CH_3 protons). Its IR spectrum (Nujol and HCB mulls) showed bands at 3055 m, 3024 w, 2980 m, 2920 w, 2900 w, 1962 vs, 1680 s, 1565 s, 1478 s, 1434 s, 1389 m, 1362 m, 1292 m, 1240 m, 1159 m, 1090 m, 1065 w, 1034 m, 1023 m, 996 w, 969 w, 869 w, 845 w, 742 s, 713 m, 692 s, 565 w, 550 w, 538 w, 513 s, 500 m, 492 m, 464 w, 444 w, 440 w, 424 w, 415 w, and 323 w cm^{-1}.

(*c*). *With acetylenedicarboxylic acid.* A mixture of the acid (0.15 g, 1.4 mmole) and the hydride (1.0 g, 1.08 mmole) in benzene (50 ml) was stirred at room temperature for 4 h to yield pale yellow crystals of [carbonylbis(triphenylphosphine)rhodio]-fumaric acid (IV) (0.6 g, 72%), which was recrystallised with some difficulty from a mixture of dichloromethane and light petroleum. [Found: C, 63.6; H, 4.6; mol.wt., 774 (benzene). $C_{41}H_{33}O_5P_2Rh$ calcd.: C, 63.9; H, 4.3%; mol.wt., 771.] This compound decomposed slowly above 190°. Its IR spectrum showed bands at 3100–2500 s(broad), 1970 vs, 1810 w, 1700 m(sh), 1690 s, 1645 s, 1575 s, 1480 s, 1430 s, 1410 w, 1310 m, 1270 m, 1210 s, 1180 m, 1155 w, 1110 w(sh), 1095 s, 1070 w, 1025 m, 995 m, 970 w, 890 w, 865 w, 845 w, 835 w, 748 s, 740 s, 720 m, 691 vs, 680 vs, 672 s, 657 w, 639 w, 615 w, 597 w, 535 s(sh), 515 vs, 510 vs, 495 s, 463 m, 450 w, 415 m, 380 w and 350 w cm^{-1}. Its ^1H NMR spectrum ($CDCl_3$, 100 MHz) showed only a multiplet at τ 2.5 for the aromatic protons, and bands due to the carboxylic acid and vinylic protons could not be detected.

(*d*). *With diphenylacetylene.* When the hydride (2.0 g, 2.16 mmole), diphenylacetylene (0.4 g, 2.2 mmole) and ether (50 ml) were sealed under vacuum in a tube (100 ml), which was then shaken at room temperature for 1 week, chromatographic separation (ether eluant) of the low melting, yellow solid residue, obtained on removal of the solvent, gave two fractions. The first of these (0.3 g) was shown by IR spectroscopy to be a mixture of triphenylphosphine and triphenylphosphine oxide. The second, on concentration of the solvent and cooling at 0° overnight gave yellow crystals of *trans*-[carbonylbis(triphenylphosphine)rhodio]stilbene (1.5 g, 82%) (V), m.p. 158° (with decomp.). (Found: C, 73.1; H, 5.2. $C_{51}H_{41}OP_2Rh$ calcd.: C, 73.4; H, 4.9%.) Its IR spectrum showed bands at 3050 w, 3030 w, 3000 w, 2960 w, 1960 vs, 1913 w, 1615 w, 1590 w, 1570 w, 1491 w, 1485 m(sh), 1477 m, 1446 w, 1435 s, 1330 w, 1310 w, 1293 w, 1182 w, 1155 w, 1118 w, 1092 m, 1089 m(sh), 1069 w, 1028 w, 1018 w, 995 w, 961 m, 956 m, 850 w, 762 m, 752 m, 739 m, 719 m, 705 m, 691 s, 560 w, 540 w, 535 w, 530 w, 520 s, 500 m, 495 m, 445 w, and 425 m cm^{-1}. Its ^1H NMR spectrum ($CDCl_3$: TMS internal reference; 100 MHz) showed bands at τ 2.8 (40, complex multiplet; aromatic protons) and 5.66 (1, singlet; vinyl proton).

(*e*). *With hexafluoro-2-butyne.* Hexafluoro-2-butyne (1.0 g, 6.16 mmole) and the hydride (2.0 g, 2.16 mmole) in ether (50 ml) were sealed under vacuum in a tube and shaken at room temperature for 3 days. Removal of the solvent and chromatographic separation of the yellow solid residue with a 1/1 mixture of ether/light petroleum as eluant gave yellow crystals of *cis*-1,1,1,3,3,3-hexafluoro-2-[carbonylbis(triphenylphosphine)rhodio]-2-butene (VI) (1.5 g, 83%), m.p. 184° (with decomp.). (Found: C, 60.0; H, 3.9; F, 13.8. $C_{41}H_{31}F_6OP_2Rh$ calcd.: C, 60.2; H, 3.8; F, 13.9%.) Its IR spectrum showed bands at 3074 m, 3056 m, 3004 m, 1985 vs, 1604 m, 1584 w, 1570 w, 1482 s, 1479 s, 1458 w, 1435 s, 1405 w, 1345 s, 1338 s, 1308 m, 1255 s, 1203 s, 1178 m, 1158 m, 1110 s, 1090 s, 1024 m, 996 m, 888 w, 844 w, 830 w, 806 m, 760 w, 745 s(sh), 740 s, 720 m, 690 s, 660 m, 637 m, 612 m, 570 m, 543 m, 510 s, 443 w, 426 w, and 417 m cm^{-1}. Its ^1H NMR spectrum ($CDCl_3$, 100 MHz) showed bands at τ 2.5 (30, complex multiplet; aromatic protons) and 5.16 [1, quartet of quartets; $J(H{-}F_{gem})$ 10.7 Hz, $J(H{-}F_{trans})$ 2.5 Hz]. The ^{19}F NMR spectrum ($CDCl_3$; TFA external reference; 56.4 MHz) showed a quartet of doublets at −27.1 ppm [3; $J(F{-}F)$ 11.2 Hz, $J(H{-}F)$ 2.5 Hz] and a quartet of doublets at −19.9 ppm [3; $J(F{-}F)$ 11.2 Hz, $J(F{-}H_{gem})$ 10.7 Hz].

Cleavage reactions with anhydrous hydrogen chloride

(*a*). *Dimethyl [carbonylbis(triphenylphosphine)rhodio] fumarate.* The adduct (I) (1.0 g, 1.02 mmole), dry hydrogen chloride (0.4 g, 11.0 mmole) and benzene (50 ml) were sealed under vacuum in a tube, which was then shaken at room temperature for 1 day. Evaporation of the solvent gave a red oil (1.0 g), which on sublimation yielded dimethyl fumarate (0.10 g, 68%) identified by IR and ^{1}H NMR spectroscopy.

(*b*). *trans-[Carbonylbis(triphenylphosphine)rhodio]stilbene.* Dry hydrogen chloride (0.5 g) was condensed *in vacuo* onto a frozen solution (−196°) of the adduct (V) (1.5 g, 1.8 mmole) in ether (50 ml) contained in a reaction tube (250 ml), which was then sealed and allowed to warm up to room temperature. The tube was then shaken for 2 days, whereupon a yellow crystalline solid had separated. This was filtered off (0.95 g) and washed with ether. This product, which was possibly a mixture of isomers of hydridodichlorocarbonylbis(triphenylphosphine)rhodium (Found: C, 60.8; H, 4.4. $C_{37}H_{31}Cl_2OP_2Rh$ calcd.: C, 61.1; H, 4.3%.) was insoluble in all common organic solvents. The filtrate was then evaporated to give a yellow solid (0.6 g), which on chromatography on Florisil (light petroleum eluant) gave white crystals of *trans*-stilbene (0.22 g, 69%) identified by IR and ^{1}H NMR spectroscopy and mixed m.p. determination with an authentic sample. Further elution with acetone gave a yellow, crystalline solid (0.2 g), shown by IR spectroscopy to be chlorocarbonylbis(triphenylphosphine)rhodium. (Found: C, 64.6; H, 4.5. $C_{37}H_{31}ClOP_2Rh$ calcd.: C, 64.2; H, 4.3%.)

REFERENCES

1 C. O'Connor and G. Wilkinson, *J. Chem. Soc. A*, (1968) 2665.
2 D. Evans, J. A. Osborn and G. Wilkinson, *J. Chem. Soc. A*, (1968) 3133.
3 M. Yagupsky and G. Wilkinson, *J. Chem. Soc. A*, (1970) 941.
4 W. Strohmeier and W. Rehder-Stirnweiss, *J. Organometal. Chem.*, 26 (1971) C23.
5 C. K. Brown and G. Wilkinson, *Tetrahedron Lett.*, (1969) 1725.
6 G. Yagupsky, C. K. Brown and G. Wilkinson, *J. Chem. Soc. A*, (1970) 1392.
7 C. K. Brown, W. Mowat, G. Yagupsky and G. Wilkinson, *J. Chem. Soc. A*, (1971) 850.
8 B. L. Booth and R. G. Hargreaves, *J. Chem. Soc. A*, (1969) 2766.
9 B. L. Booth and R. G. Hargreaves, *J. Organometal. Chem.*, 33 (1971) 365.
10 W. H. Baddley and M. S. Fraser, *J. Amer. Chem. Soc.*, 91 (1969) 3661.
11 M. C. Baird, J. T. Mague, J. A. Osborn and G. Wilkinson, *J. Chem. Soc. A*, (1967) 1347.
12 P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, 1 (1964) 192.
13 B. L. Booth and R. G. Hargreaves, *J. Chem. Soc. A*, (1970) 308.
14 W. Hieber and V. Frey, *Chem. Ber.*, 99 (1969) 2614.
15 H. C. Clark and W. S. Tsang, *J. Amer. Chem. Soc.*, 89 (1967) 533.
16 W. Cullen, D. S. Dawson and G. E. Styan, *Can. J. Chem.*, 43 (1965) 3392.
17 J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution NMR Spectroscopy*, Vol. 2, Pergammon Press, 1966, p. 913.
18 D. Evans, G. Yagupsky and G. Wilkinson, *J. Chem. Soc. A*, (1968) 2660.
19 J. B. Wilford, A. Forster and F. G. A. Stone, *J. Chem. Soc.*, (1965) 6519; P. M. Treichel, E. Pitcher and F. G. A. Stone, *Inorg. Chem.*, 1 (1962) 511; J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, 4 (1965) 93; J. B. Wilford, P. M. Treichel and F. G. A. Stone, *J. Organometal. Chem.*, 2 (1964) 119; D. A. Harbourne and F. G. A. Stone, *J. Chem. Soc. A*, (1968) 1765.
20 M. I. Bruce and W. R. Cullen, *Fluorine Chem. Rev.*, 4 (1969) 98.
21 C. G. Krespan, R. J. Harder and J. J. Drysdale, *J. Chem. Soc.*, (1951) 584.
22 B. S. Rabinovitch and F. S. Looney, *J. Amer. Chem. Soc.*, 75 (1953) 2652.