Trimethylenemethane Metal Complexes. Part 1. Synthesis of Ruthenium, Osmium, Rhodium, and Iridium Complexes†

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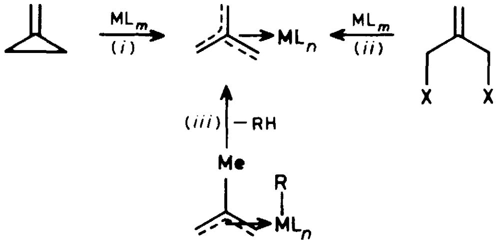
2-[(Methylsulphonyloxy)methyl]-3-trimethylsilylprop-1-ene, available from 2-methylprop-2-en-1-ol, serves as a new entry into trimethylenemethane (tmm) metal complexes. Reaction with low-valent metal complexes affords the first tmm metal complexes of ruthenium, osmium, rhodium, and iridium: $[MCl(NO)(PPh_3)(\eta^4\text{-tmm})]$ (M = Ru or Os), $[Os(CO)_2(PPh_3)(\eta^4\text{-tmm})]$, $[MCl(PPh_3)_2(\eta^4\text{-tmm})]$ (M = Rh or Ir), and $[IrX(CO)(L)(\eta^4\text{-tmm})]$ (X = Cl, L = PPh_3 or $AsPh_3$; X = Br, L = PPh_3). The desilylation of an η^3-allyl intermediate rationalises the results and has been verified by the reaction of sodium fluoride with $[Rh\{\eta^3\text{-}CH_2C(CH_2SiMe_3)CH_2\}Cl(CO)(PMe_2Ph)_2]BPh_4$ in aqueous methyl cyanide which gave the complex $[Rh(CO)(PMe_2Ph)_2(\eta^4\text{-tmm})]BPh_4$ in quantitative yield. N.m.r. data (^1H, $^{13}C\text{-}\{^1H\}$) are reported and variable-temperature ^1H n.m.r. spin-magnetisation transfer experiments have been used to set a lower limit of *ca.* 90 kJ mol^{-1} for the activation energies for trimethylenemethane rotation.

Trimethylenemethane (tmm) metal complexes have been synthesised *via* three main routes (Scheme 1): (*i*) the ring opening of alkylidenecyclopropanes,[1–4] (*ii*) the dehalogenation of α,α′-dihalogeno-substituted precursors,[5,6] and (*iii*) the thermal extrusion of RH (R = Cl[5] or Me[7]) from methylallyl complexes. The ability of palladium(0) catalysts to mediate the cyclo-addition of the trimethylenemethane fragment to alkenes,[8] Scheme 2, led us to investigate the reactions of $Me_3SiCH_2C(=CH_2)CH_2O_2CMe$ (**1a**) and its derivatives with other low-valent metal complexes. In preliminary communications[9,10] we have shown that derivatives of (**1a**) react with low-valent metal centres to form η^4-tmm complexes and in this paper we give full details of these reactions.



Scheme 1. X = halide, R = Cl or Me

Results and Discussion

Inspired by the ability of the allylic acetate (**1a**) to eliminate trimethylsilyl acetate in the presence of palladium(0) catalysts[8] we observed that *trans*-$[IrCl(CO)(PPh_3)_2]$ and the allylic chloride $Me_3SiCH_2C(=CH_2)CH_2Cl$ (**1b**) in refluxing toluene gave a small yield of the η^4-tmm complex $[IrCl(CO)(PPh_3)(\eta^4\text{-tmm})]$ (**2**), Scheme 3. Following the pathway proposed for the formation of the reactive intermediate $[Pd(\eta^3\text{-tmm})(PPh_3)_2]$[8] a plausible route to (**2**) may involve oxidative addition of the allylic chloride (**1b**) to the co-ordinatively unsaturated iridium centre to give a σ-allyl, formation of an η^3-allyl, and elimination of $SiMe_3Cl$ from the η^3-allyl intermediate (**3**), Scheme 4. A crucial step in this mechanism is the ionisation of chloride from the metal centre followed by attack of chloride at silicon to effect desilylation of the η^3-allyl complex (**3**). The ability of allylic methanesulphonates oxidatively to add rapidly to iridium(I) centres coupled with the poor co-ordinating ability of the methanesulphonate group[11] suggested that the methanesulphonate $Me_3SiCH_2C(=CH_2)CH_2OS(O)_2Me$ (**1c**) might be an attractive precursor to tmm metal complexes. Accordingly the reactions of (**1c**) with a number of low-valent iridium complexes were investigated. These reactions afforded much improved yields of a variety of η^4-tmm complexes of iridium and the results are summarised in the Table.

A reaction of interest is that of (**1c**) with $[IrH(CO)(PPh_3)_3]$ which affords the cationic tmm complex $[Ir(CO)(PPh_3)_2(\eta^4\text{-tmm})][OS(O)_2Me]$ (**4**) in high yield. Elimination of $SiMe_3H$ from an intermediate of the type (**5**, M = Ir) provides an attractive pathway to the tmm complex (**4**), Scheme 5. Complex (**4**) was also formed in the reaction of the chloride (**1b**) with *trans*-$[IrCl(CO)(PPh_3)_2]$ in the presence of KPF_6.

In an attempt to obtain the cationic tmm rhodium analogue of (**4**) the action of the methanesulphonate (**1c**) upon $[RhH(CO)PPh_3)_3]$ was also investigated. However, this reaction gave *trans*-$[Rh\{OS(O)_2Me\}(CO)(PPh_3)_2]$ presumably because reductive elimination of $Me_3SiCH_2C(Me)=CH_2$ occurs in preference to either elimination of $SiMe_3H$ or desilylation of the η^3-trimethylsilylmethylallyl intermediate (**5**, M = Rh).

Previous studies have shown that oxidative addition of allyl halides to *trans*-$[MCl(CO)(PMe_2Ph)_2]$ (M = Rh or Ir)[12,13] gives octahedral σ-allyl complexes which on treatment with $NaBPh_4$ afford cationic η^3-allyl derivatives. We similarly found that the methanesulphonate (**1c**) reacted with *trans*-$[RhCl(CO)(PMe_2Ph)_2]$ in the presence of $NaBPh_4$ to give the cationic trimethylsilylmethylallyl complex $[Rh\{\eta^3\text{-}CH_2C(CH_2SiMe_3)CH_2\}Cl(CO)(PMe_2Ph)_2]BPh_4$ (**6**) in high yield. The analogous iridium complex could not be isolated. The reaction of (**1c**) with *trans*-$[IrCl(CO)(PMe_2Ph)_2]$ in the presence of $NaBPh_4$ afforded the protodesilylated product $[Ir\{\eta^3\text{-}CH_2C(Me)CH_2\}Cl(CO)(PMe_2Ph)_2]BPh_4$ (**7**). A plausible explanation for this difference is that after initial oxidative addition of the methanesulphonate (**1c**) to the metal centre there exists an ion pair (**8**), Scheme 6. Attack by the methanesulphonate anion at the trimethylsilyl group will lead to the protodesilylated product [step (*i*)] or alternatively, attack at the metal will lead to a σ-allyl [step (*ii*)]. Addition of $NaBPh_4$ affords the respective η^3-allyls. The attack of the anion at the metal centre requires prior dissociation of the co-ordinated solvent molecule (S). Such a process is many times

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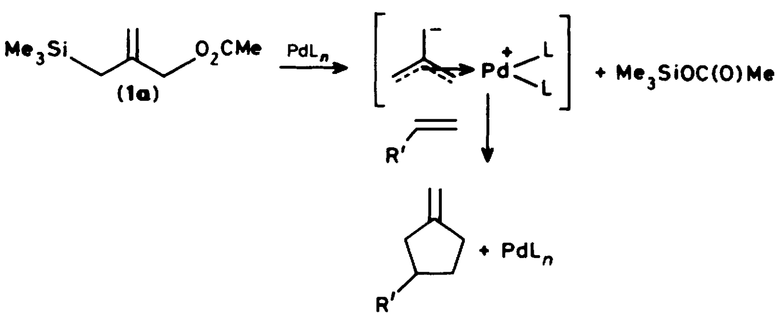
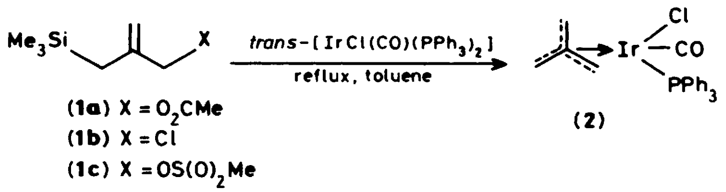
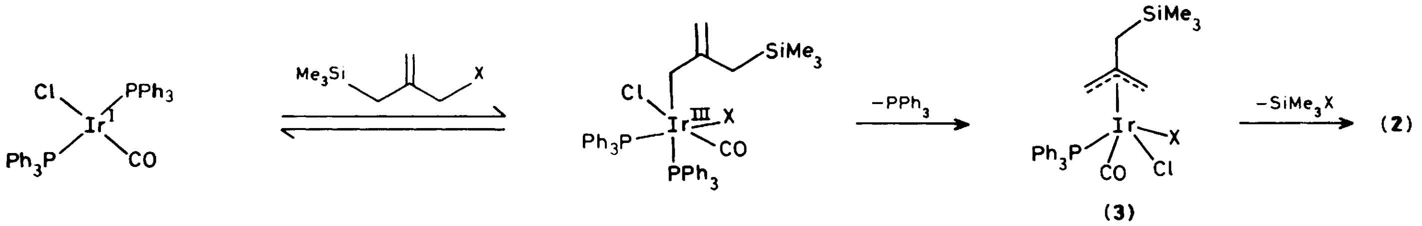
* *Non-S.I. units employed:* mmHg = 133 Nm^{-2}, eV = 1.60 × 10^{-19} J.



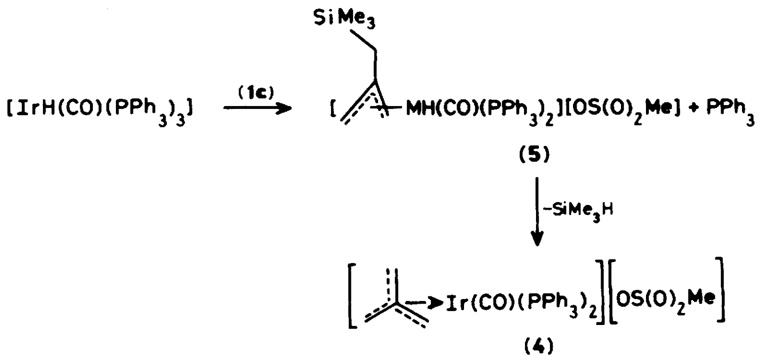
Scheme 2. R′ = electron withdrawing group



Scheme 3.



Scheme 4. X = Cl or OS(O)$_2$Me



Scheme 5.

slower at an iridium(III) centre as compared to corresponding rhodium(III) centres.[14] Thus in the iridium system attack by methanesulphonate at silicon is preferred to slower attack at the metal.

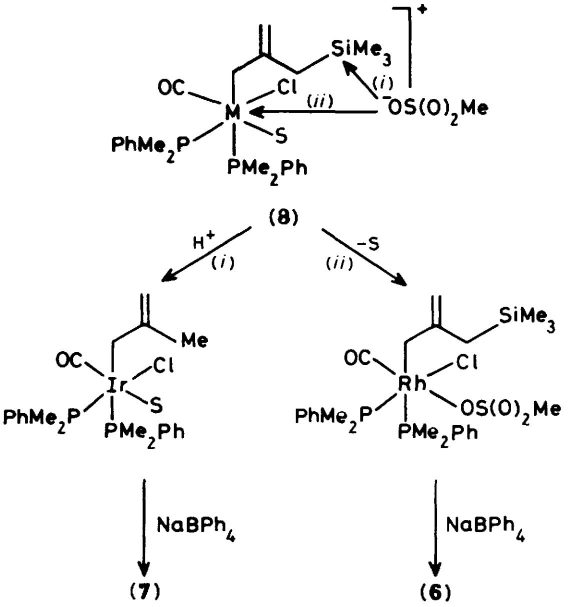
Complex [Rh{η^3-CH$_2$C(CH$_2$SiMe$_3$)CH$_2$}Cl(CO)(PMe$_2$Ph)$_2$]BPh$_4$ (**6**) was readily desilylated by sodium fluoride in aqueous methyl cyanide to give a quantitative yield of the cationic rhodium tmm complex [Rh(CO)(PMe$_2$Ph)$_2$(η^4-tmm)]BPh$_4$ (**9**). Interestingly these conditions could have led to protodesilylation. However, loss of SiMe$_3$F from the cationic η^3-allyl (**6**) in the presence of sodium fluoride would lead to a neutral species (Scheme 7) which would be less prone to protonation than for example the anionic system involved in protodesilylation of [Mo(≡CCH$_2$SiMe$_3$){P(OMe)$_3$}$_2$(η^5-indenyl)].[15,16] The formation of the cationic tmm rhodium complex (**9**) provides good evidence for the proposed mechanism of formation of the tmm metal complexes, that is initial oxidative addition to the low-valent metal centre followed by elimination of SiMe$_3$X (X = Cl or F) from the intermediate η^3-allyl, Scheme 4. However, we note that elimination of SiMe$_3$X from a σ-allyl, formed by attack of fluoride at the metal, is also possible.

A number of other iridium and rhodium trimethylenemethane metal complexes have been synthesised and these results are

Table. Synthesis of trimethylenemethane metal complexes

Substrate	(1) mol	Solvent	T/°C	Time/h	Product	Yield (%)
$[IrCl(CO)(PPh_3)_2]$	3^a	PhMe	110	12	$[IrCl(CO)(PPh_3)(\eta^4\text{-tmm})]$	11
$[IrCl(CO)(PPh_3)_2]$	3^b	PhMe	110	12	$[IrCl(CO)(PPh_3)(\eta^4\text{-tmm})]$	75
$[IrBr(CO)(PPh_3)_2]$	3^b	PhMe	110	6	$[IrBr(CO)(PPh_3)(\eta^4\text{-tmm})]$	76
$[IrCl(CO)(AsPh_3)_2]$	3^b	PhMe	110	0.5	$[IrCl(CO)(AsPh_3)(\eta^4\text{-tmm})]$	77
$[IrCl(CO)(PPh_3)_2]$	3^a	PhMe–MeCN	Reflux	12	$[Ir(CO)(PPh_3)_2(\eta^4\text{-tmm})]PF_6$	60
$[IrH(CO)(PPh_3)_3]$	3^b	PhMe	*ca.* 80	*ca.* 1	$[Ir(CO)(PPh_3)_2(\eta^4\text{-tmm})][OS(O)_2Me]$	90
$[Ir_2Cl_2(C_8H_{14})_4]$–4PPh$_3$	2.2^b	C_6H_6	80	1.5	$[IrCl(PPh_3)_2(\eta^4\text{-tmm})]$	45
$[RhCl(PPh_3)_3]$	8^b	C_6H_6	*ca.* 70	0.05	$[RhCl(PPh_3)_2(\eta^4\text{-tmm})]$	50
$[Os(CO)_2(PPh_3)_3]$	3^c	C_6H_6	80	12	$[Os(CO)_2(PPh_3)(\eta^4\text{-tmm})]$	11
$[Os(CO)_2(PPh_3)_3]$	3^b	C_6H_6	80	12	$[Os(CO)_2(PPh_3)(\eta^4\text{-tmm})]$	35
$[OsCl(NO)(PPh_3)_3]$	3^b	C_6H_6	20	0.5	$[OsCl(NO)(PPh_3)(\eta^4\text{-tmm})]$	20
$[RuCl(NO)(PPh_3)_2]$	3^b	C_6H_6	20	14	$[RuCl(NO)(PPh_3)(\eta^4\text{-tmm})]$	20

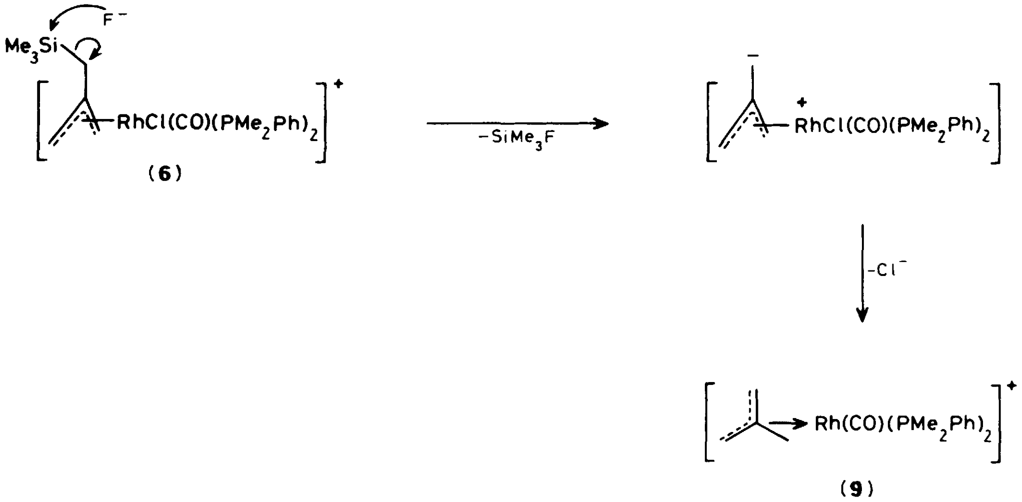
[a] Reagent (**1b**). [b] Reagent (**1c**). [c] Reagent (**1a**).



Scheme 6. S = solvent

summarised in the Table along with the first trimethylenemethane complexes of ruthenium and osmium. An excess of the methanesulphonate (**1c**) is used in these syntheses in order to overcome any loss of (**1c**) by quaternisation of liberated triphenylphosphine.

Single-crystal *X*-ray structural studies of $[IrCl(CO)(PPh_3)(\eta^4\text{-tmm})]$[9] and several other complexes[17] establish that the union of the tmm ligand with the $[IrCl(CO)(PPh_3)]$ and other ML_3 metal fragments creates a distorted octahedral arrangement about the metal with the methylene carbon atoms occupying three facial vertices as predicted by theoretical considerations.[18,19] The n.m.r. spectra of the complexes are consistent with this staggered conformation, the data indicating that the tmm ligand is rigid and that no rotation occurs on the n.m.r. time-scale at room temperature. Thus the ^1H n.m.r. spectrum of $[IrCl(CO)(PPh_3)(\eta^4\text{-tmm})]$ (**2**), measured at room temperature, shows six resonances due to the methylene protons of the co-ordinated tmm, Figure. Rotation of the tmm ligand would equilibriate all six protons. Each proton of tmm in (**2**) shows long range ^1H–^1H 'W-coupling', *e.g.* H^2 couples strongly to H^5. In addition H^5, H^6, H^2, and H^3 show additional coupling to phosphorus. The protons H^5 and H^6, which are in a pseudo *trans* orientation with respect to phosphorus, exhibit the larger ^{31}P–^1H coupling. H^1 and H^4 show no coupling to phosphorus. This full analysis of the spectrum has been



Scheme 7.

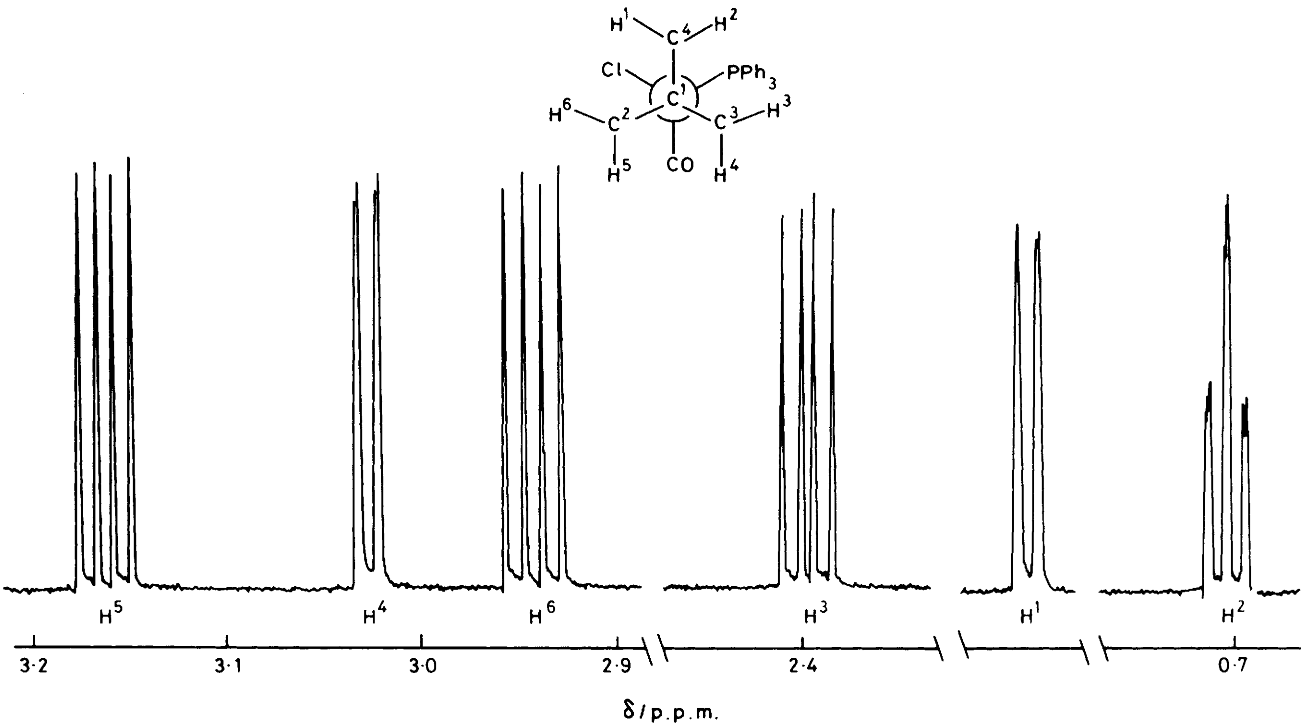
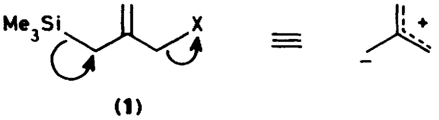


Figure. ^{1}H N.m.r. spectrum of [IrCl(CO)(PPh$_3$)(η^4-tmm)] (**2**) at room temperature. The complex is viewed along the C^1 metal axis



(**1**)

Scheme 8.

obtained from selective decoupling experiments and nuclear Overhauser enhancement (n.O.e.) difference spectra. Thus n.O.e. is observed for pairs of protons which are geminally related, *e.g.* H^1 and H^2, and also for a weaker, longer range interaction, *e.g.* H^1 and H^6. The n.O.e. technique not only provides the full assignment of the tmm fragment but due to the close proximity of H^2 and H^3 with the *ortho* protons of the triphenylphosphine rings it is possible to obtain the arrangement of the other ligands relative to the tmm protons. Similar information can be obtained for the other tmm complexes.

The ^{13}C n.m.r. spectra of the tmm metal complexes show the expected characteristic resonance due to the central carbon C^1 in the region 100—114 p.p.m.[1,17] This resonance also exhibits a small coupling to co-ordinated tertiary phosphine ligands of the order of 1—3 Hz. Larger ^{13}C–^{31}P couplings are observed for methylene carbons *trans* to phosphorus ligands. Thus the methylene carbon (C^2) *trans* to phosphorus in [IrCl(CO)(PPh$_3$)(η^4-tmm)] (**2**) exhibits a ^{13}C–^{31}P coupling of 38 Hz. Both C^3 and C^4 show no coupling to phosphorus.

The tmm ligand in (**2**) is also rigid at 70 °C on the n.m.r. time-scale. Thus no sign of rotation of the tmm ligand could be detected by a spin-magnetisation transfer experiment at 70 °C giving a lower limit for $\Delta G^‡$ for this process of the order of 90 kJ mol^{-1}. The osmium complex [Os(CO)$_2$(PPh$_3$)(η^4-tmm)] was heated to 100 °C and again no spin-magnetisation transfer could be observed, setting the lower limit of $\Delta G^‡$ for this process at 95 kJ mol^{-1}. Both of these values are higher than the range (71—79 kJ mol^{-1}) found for the rotational barriers of the substituted tmm complexes [Fe(CO)$_3${η^4-C(CHR)(CH$_2$)$_2$}] [R = COMe, MeCH(OH), MeCH(O$_2$CMe), or Et].[20] The origins of the barrier to rotation in tmm metal complexes have been well documented, and a large increase in the barrier of rotation would be expected on replacing carbonyls with tertiary phosphine or chloride ligands,[18,19] as well as descending to second- and third-row '*d*-block' transition metals.

In summary the method developed by Trost and Chan[8] and extended herein represents a general approach to the synthesis of a number of η^4-tmm metal complexes using the 'push-pull' precursors (**1**) (Scheme 8).

Experimental

Melting points were measured on a Reichert hot-stage apparatus and are uncorrected. Infrared spectra were recorded as CsCl discs on a Perkin-Elmer 580 spectrophotometer. Hydrogen-1 n.m.r. were recorded on a Bruker Spectrospin WH 400 spectrometer at 400.13 MHz, a JEOL EM390 spectrometer at 90 MHz, and a Bruker AM300 spectrometer at 300.13 MHz with SiMe$_4$ (0.0 p.p.m.) as internal reference, positive values being to high frequency (low field) in [^{2}H$_2$]dichloromethane unless otherwise stated; coupling constants are in Hz. Carbon-13, hydrogen-1 decoupled, n.m.r. spectra were recorded on a Bruker Spectrospin WH400 spectrometer at 100.62 MHz and on a Bruker AM 300 spectrometer at 75.47 MHz with SiMe$_4$ (0.0 p.p.m.) as internal reference. The carbon-13 data for the aromatic region have been omitted for clarity. Phosphorus-31, hydrogen-1 decoupled, n.m.r. spectra were recorded on a JEOL JNM-FX60 spectrometer at 24.15 MHz with [P(OH)$_4$]$^+$ in D$_2$O (0.0 p.p.m.) as external reference.[21] Mass spectra were obtained using an A.E.I. MS9 spectrometer at 70 eV.

Experiments were carried out under a dry, oxygen-free nitrogen atmosphere, using solvents which were dried and distilled under nitrogen prior to use. The compounds *trans*-[IrCl(CO)(PPh$_3$)$_2$],[22] [IrH(CO)(PPh$_3$)$_3$],[23] [RhH(CO)-

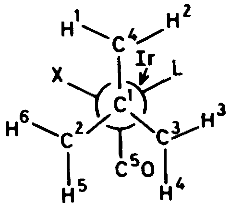
$(PPh_3)_3]$,[24] *trans*-$[RhCl(CO)(PMe_2Ph)_2]$,[25] *trans*-$[IrCl(CO)(PMe_2Ph)_2]$,[26] *trans*-$[IrBr(CO)(PPh_3)_2]$,[27] *trans*-$[IrCl(CO)(AsPh_3)_2]$,[28] $[Ir_2Cl_2(C_8H_{14})_4]$,[29] $[RhCl(PPh_3)_3]$,[30] $[Os(CO)_2(PPh_3)_3]$,[31] $[OsCl(NO)(PPh_3)_3]$,[32] $[RuCl(NO)(PPh_3)_2]$,[33] 2-(hydroxymethyl)-3-trimethylsilylprop-1-ene,[34] and 2-(acetoxymethyl)-3-trimethylsilylprop-1-ene[8] were prepared as described in the literature. Light petroleum refers to that fraction of b.p. 40—60 °C.

Preparation of 2-[(*Methylsulphonyloxy*)*methyl*]-3-*trimethylsilylprop*-1-*ene* (**1c**).—Methanesulphonyl chloride (1.66 g, 0.144 mol) in dichloromethane (15 cm^3) was added dropwise over 0.5 h to a stirred solution of 2-(hydroxymethyl)-3-trimethylsilylprop-1-ene (2.0 g, 0.0133 mol) and triethylamine (3.0 g, 0.03 mol) in dichloromethane (10 cm^3) at 0 °C. The resultant cloudy solution was stirred at 0 °C for a further 0.5 h. The reaction mixture was diluted with diethyl ether (50 cm^3), washed successively with saturated sodium bicarbonate (2 × 25 cm^3), saturated copper sulphate (3 × 25 cm^3), water (25 cm^3), and brine (25 cm^3) and dried over anhydrous potassium carbonate. The solvent was removed at water pump pressure and the residue distilled (80 °C, 0.5 mmHg) to give 2.76 g (90%) of the title compound as a colourless liquid. N.m.r. ($CDCl_3$): ^1H (90 MHz), δ 0.1 (s, 9 H), 1.6 (s, 2 H), 3.0 (s, 3 H), 4.5 (br s, 2 H), 4.8 (br s, 1 H), and 5.0 (m, 1 H). I.r. (film): 3 080w, 3 030w, 2 950m, 2 920m, 1 640m, 1 460m, 1 420m, 1 360s, 1 255s, 1 175vs, 1 010s, 970s, 935s, and 855vs cm^{-1}. Mass spectrum, *m*/*e* (%) M^+ 222 (6), 169 (10), 155 (5), 154 (6), 153 (100), 110 (10).

Preparation of 2-(*Chloromethyl*)-3-*trimethylsilylprop*-1-*ene* (**1b**).—Thionyl chloride (1.7 g, 14 mmol) in dichloromethane (100 cm^3) was added dropwise to a stirred solution of 2-(hydroxymethyl)-3-trimethylsilylprop-1-ene (2.0 g, 13.86 mmol) and pyridine (1.5 g, 18.9 mmol) in dichloromethane (100 cm^3) at 0 °C. The solution was stirred for 0.5 h at 0 °C and then allowed to warm to room temperature and stirred for a further 0.5 h. The solution was washed with dilute sulphuric acid (0.1 mol dm^{-3}, 3 × 100 cm^3) and dried over anhydrous potassium carbonate. The solvent was removed *in vacuo* and the residue distilled (40 °C, 0.005 mmHg) into a trap cooled to −78 °C to give a clear oil (2.21 g, 98%). The product must be stored at 0 °C to avoid decomposition. N.m.r. ($CDCl_3$): ^1H (90 MHz), δ 0.1 (s, 9 H, $SiMe_3$), 1.7 (s, 2 H, CH_2SiMe_3), 4.4 (br s, 2 H, CH_2Cl), 4.85 (br s, 1 H), 5.0 (m, 1 H). I.r. (film): 850 cm^{-1}.

Preparation of Trimethylenemethane Metal Complexes.—*Carbonylchloro*(η^4-*trimethylenemethane*)(*triphenylphosphine*)-*iridium* (**2**). *trans*-$[IrCl(CO)(PPh_3)_2]$ (1.00 g, 1.28 mmol) and 2-[(methylsulphonyloxy)methyl]-3-trimethylsilylprop-1-ene (**1c**) (0.85 g, 3.84 mmol) in toluene (20 cm^3) were refluxed for 12 h (the reaction appeared to be complete after the disappearance of the yellow colour within 3 h). The solvent was removed *in vacuo* and ethanol (5 cm^3) was added to the residue. The white product was filtered off and washed with ethanol (5 cm^3) and diethyl ether (5 cm^3). The product was recrystallised from hot ethanol (0.55 g, 0.96 mmol, 75%), m.p. >180 °C (decomp.) (Found: C, 48.2; H, 3.6. $C_{23}H_{21}ClIrOP$ requires C, 48.3; H, 3.7%). I.r.: ν_{CO} 2 030, ν_{IrCl} 282 cm^{-1}. N.m.r. (C_6D_6): ^1H (400 MHz), δ 0.70 [dt, 1 H, H^2, $J(H^2H^5) = J(H^2P) = 3.8$, $J(H^2H^1)$ 0.7], 1.66 [br, d, 1 H, H^1, $J(H^1H^4)$ 4.1], 2.40 [dd, 1 H, H^3, $J(H^3H^6)$ 3.9, $J(H^3P)$ 6.4], 2.94 [dd, 1 H, H^6, $J(H^6H^3)$ 3.9, $J(H^6P)$ 7.5], 3.03 [dd, 1 H, H^4, $J(H^4H^1)$ 4.1, $J(H^4H^3)$ or $J(H^4P)$ 0.5], 3.16 [dd, 1 H, H^5, $J(H^5H^2)$] 3.8, $J(H^5P)$ 7.0], and 7.55 (m, 15 H, PPh_3); ^{13}C-{^1H} (100 MHz), δ 40.2 (s, C^3), 54.0 [d, C^2, $J(C^2P)$ 37.7], 57.8 (s, C^4), 108.8 [d, C^1, $J(C^1P)$ 3.1], and 175.0 p.p.m. [d, C^5, $J(C^5P)$ 4.4]; ^{31}P-{^1H} ($CDCl_3$), δ 6.25 p.p.m.

Bromo(*carbonyl*)(η^4-*trimethylenemethane*)(*triphenylphosphine*)*iridium*. *trans*-$[IrBr(CO)(PPh_3)_2]$ (0.50 g, 0.60 mmol) and (**1c**) (0.4 g, 1.82 mmol) were refluxed in toluene (10 cm^3) for 6 h. The solvent was removed *in vacuo* and ethanol (5 cm^3) was added to the residue. The white precipitate was filtered off and washed with ethanol (3 cm^3) and diethyl ether (5 cm^3). Yield: 0.28 g (0.45 mmol, 76%), m.p. >170 °C (decomp.) (Found: C, 44.9; H, 3.5. $C_{23}H_{21}BrIrOP$ requires C, 44.8; H, 3.4%). I.r.: ν_{CO} 2 030 cm^{-1}. N.m.r. (CD_2Cl_2): ^1H (400 MHz), δ 1.14 [t, 1 H, H^2, $J(H^2H^5) = J(H^2P) = 3.7$], 2.29 [br d, 1 H, H^1, $J(H^1H^4)$ 4.13], 2.42 [dd, 1 H, H^3, $J(H^3H^6)$ 3.95, $J(H^3P)$ 6.29], 2.99 [d, 1 H, H^4, $J(H^4H^1)$ 4.13], 3.08 [dd, 1 H, H^5, $J(H^5H^2)$ 3.7, $J(H^5P)$ 6.84], 3.18 [dd, 1 H, H^6, $J(H^6H^3)$ 3.95, $J(H^6P)$ 7.39], and 7.55 (m, 15 H, PPh_3); ^{13}C-{^1H} (100 MHz), δ 43.8 (s, C^3), 52.99 [d, C^2, $J(C^2P)$ 36.5] 57.00 (s, C^4), 107.88 (s, C^1), and 173.98 p.p.m. (s, C^5).

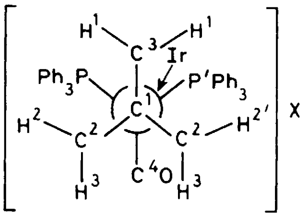


	X	L
(2)	Cl	PPh_3
	Br	PPh_3
	Cl	$AsPh_3$

Carbonylchloro(η^4-*trimethylenemethane*)(*triphenylarsine*)-*iridium*. *trans*-$[IrCl(CO)(AsPh_3)_2]$ (0.33 g, 0.374 mmol) and (**1c**) (0.255 g, 1.14 mmol) in toluene (15 cm^3) were warmed to reflux for 0.5 h. After cooling the solvent was removed *in vacuo* and diethyl ether (10 cm^3) was added. The cream coloured compound was filtered off and washed with diethyl ether (10 cm^3) and dried *in vacuo* to give the title complex (0.177 g, 77%), m.p. >138 °C (decomp.) (Found: C, 44.6; H, 3.4. $C_{23}H_{21}AsClIrO$ requires C, 44.8; H, 3.4%). I.r.: ν_{CO} 2 020, ν_{IrCl} 285 cm^{-1}. N.m.r. (CD_2Cl_2): ^1H (400 MHz), δ 1.54 [d, 1 H, H^2, $J(H^2H^5)$ 3.46], 2.11 [d, 1 H, H^1, $J(H^1H^4)$ 4.10], 2.72 [d, 1 H, H^3, $J(H^3H^6)$ 3.92], 2.88 [d, 1 H, H^4, $J(H^4H^1)$ 4.10], 3.12 [d, 1 H, H^5, $J(H^5H^2)$ 3.46], 3.19 [d, 1 H, H^6, $J(H^6H^3)$ 3.92], and 7.5 (m, 15 H, $AsPh_3$); ^{13}C-{^1H} (100 MHz), δ 37.44 (s, C^3), 52.05 (s, C^2), 57.18 (s, C^4), 106.07 (s, C^1), and 174.4 p.p.m. (s, C^5).

Carbonyl(η^4-*trimethylenemethane*)*bis*(*triphenylphosphine*)-*iridium methanesulphonate* (**4**). $[IrH(CO)(PPh_3)_3]$ (0.46 g, 0.45 mmol) and (**1c**) (0.31 g, 1.39 mmol) were warmed in toluene (15 cm^3) until complete formation of the white solid had occurred (*ca.* 1 h). The solution was cooled and the product was filtered off and washed with light petroleum (15 cm^3) to give the title complex (0.36 g, 90%). Recrystallisation from dichloromethane and light petroleum afforded white needles which crystallised with 0.75 mol equiv. of dichloromethane (as seen by ^1H n.m.r.), m.p. 107—109 °C (Found: C, 53.4; H, 4.6. $C_{42}H_{39}IrO_4P_2S \cdot 0.75CH_2Cl_2$ requires C, 53.6; H, 4.3%). I.r.: ν_{CO} 2 040 cm^{-1}. N.m.r. ($CDCl_3$): ^1H (90 MHz), δ 2.0 [1:2:6:2:1 quintet, 2 H, H^2, AA′XX′ system, $J(H^2H^{2'})$ 4.1, $J(PP')$ 0.0, $J(H^2P) = -J(H^{2'}P) = \pm 5.8$], 2.3 [dd, 2 H, H^1, $J(H^1H^3)$ 4.1, $J(H^1P)$ 6.5], 2.8 [s, 3 H, $MeSO_3$], 3.3 [dd, 2 H, H^3, $J(H^3H^1)$ 4.1, $J(H^3P)$ 6.4], and 7.5 (m, 30 H, PPh_3); ^{31}P-{^1H}, δ −2.42 p.p.m.

Carbonyl(η^4-*trimethylenemethane*)*bis*(*triphenylphosphine*)-*iridium hexafluorophosphate*. *trans*-$[IrCl(CO)(PPh_3)_2]$ (1.0 g, 1.28 mmol), KPF_6 (0.37 g, 2.0 mmol), and (**1b**) (0.6 g, 3.69 mmol) in methyl cyanide (20 cm^3) and toluene (20 cm^3) were refluxed for 12 h. The solvent was removed *in vacuo* and the residue dissolved in methyl cyanide (30 cm^3) and unchanged *trans*-$[IrCl(CO)(PPh_3)_2]$ (0.16 g, 0.2 mmol) was filtered off. The



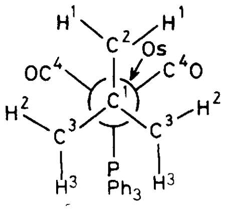
X

(4) $OS(O)_2Me$

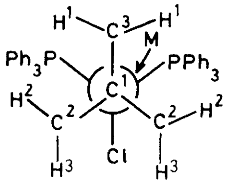
PF_6

solvent was removed *in vacuo*, the residue was dissolved in dichloromethane (20 cm^3) and potassium salts were filtered off. The solvent was removed *in vacuo* and the product recrystallised from hot ethanol to give the title complex (0.7 g, 0.74 mmol, 58%) (Found: C, 51.7; H, 4.0. $C_{41}H_{36}F_6IrOP_3$ requires C, 52.2; H, 3.8%). I.r.: ν_{CO} 2 040 cm^{-1}. N.m.r. (CD_2Cl_2): ^{1}H (400 MHz), δ 2.02 [1:2:6:2:1 quintet, 2 H, H^2, AA′XX′ system, J(H^{2}H$^{2'}$) 4.1, J(PP′) 0, J(H^{2}P) = $-J$(H$^{2'}$P) = $\pm$5.8], 2.27 [dd, 2 H, H^1, J(H^{1}H^3) 4.1, J(H^{1}P) 6.5], 3.26 [dd, 2 H, H^3, J(H^{3}H^1) 4.1, J(H^{3}P) 6.4], and 7.5 (m, 30 H, PPh$_3$); ^{13}C-{^{1}H} (100 MHz), δ 54.9 [d, C^2, J(C^{2}P) 29.8], 58.5 (s, C^3), 108.2 (s, C^1), and 172.2 p.p.m. (s, C^4).

Dicarbonyl(η^4-*trimethylenemethane*)(*triphenylphosphine*)-*osmium*. A suspension of [Os(CO)$_2$(PPh$_3$)$_3$] (0.8 g, 0.77 mmol) in benzene (15 cm^3) and (**1c**) (0.57 g, 2.56 mmol) were refluxed for 12 h. A white solid was filtered off (0.185 g) (which has yet to be identified). The solvent was removed *in vacuo* from the mother-liquor and methanol (5 cm^3) was added to the oily residue. The white product was filtered off and washed with methanol (5 cm^3) and light petroleum (10 cm^3). Yield: 0.16 g (35%), m.p. 145 °C (Found: C, 50.8; H, 3.6. $C_{24}H_{21}O_2OsP$ requires C, 51.2; H, 3.7%). I.r.: ν_{CO} 2 000, 1 935 cm^{-1}. N.m.r. (CD_2Cl_2): ^{1}H (400 MHz), δ 1.04 [dd, 2 H, H^1, J(H^{1}H^3) 4.2, J(H^{1}P) 6.65], 2.06 (s, 2 H, H^2), 2.07 [t, 2 H, H^3, J(H^{3}H^1) = J(H^{3}P) = 4.2], and 7.5 (m, 15 H, PPh$_3$); ^{13}C-{^{1}H} (100 MHz), δ 34.44 [d, C^2, J(C^{2}P) 23.2], 44.11 [d, C^3, J(C^{3}P) 2.46], 107.51 (s, C^1), and 185.2 p.p.m. [d, C^4, J(C^{4}P) 2.42].



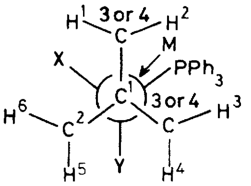
Chloro(η^4-*trimethylenemethane*)*bis*(*triphenylphosphine*)*iridium*. A solution of [Ir$_2$Cl$_2$(C$_8$H$_{14}$)$_4$] (0.5 g, 0.56 mmol) and PPh$_3$ (0.58 g, 2.21 mmol) were stirred under N$_2$ in benzene (40 cm^3). After 5 min (**1c**) (0.383 g, 1.72 mmol) was added under N$_2$. The solution was heated to reflux for 1.5 h. The solvent was removed *in vacuo* and the residue was washed with light petroleum and chromatographed on alumina. Elution with dichloromethane gave a pale yellow band. Recrystallisation from CH$_2$Cl$_2$–light petroleum gave large crystals of the title complex (0.41 g, 0.51 mmol, 45%), m.p. 200 °C (decomp.) (Found C, 59.3; H, 4.9. $C_{40}H_{36}ClIrP_2$ requires C, 59.6; H, 4.5%). I.r.: ν_{IrCl} 260 cm^{-1}. N.m.r. (CD_2Cl_2): ^{1}H (400 MHz), δ 0.81 [t, 2 H, H^1, J(H^{1}H^3) = J(H^{1}P) = 3.8], 2.1 [1:2:4:4:2:1 sextet, 2 H, H^2, AA′XX′ system, J(H^{2}H$^{2'}$) 3.7, J(PP′) 0.0, J(H^{2}P) 6.65, J(H^{2}P′) $-$5.3], 2.9 [dd, 2 H, H^3, J(H^{3}H^1) 3.8, J(H^{3}P) 6.96], and 7.55 (m, 30 H, PPh$_3$): ^{13}C-{^{1}H}, (100 MHz), δ 39.0 (s, C^2), 55.3 [dd, AXX′, |J(C^{2}P) + J(C^{2}P′)| 42.6, J(PP′) 0], and 104.5 p.p.m. [t, C^1, J(C^{1}P) 3.0]; ^{31}P-{^{1}H}, δ 0.201 p.p.m. (s).



M = Ir or Rh

Chloro(η^4-*trimethylenemethane*)*bis*(*triphenylphosphine*)*rhodium*. A solution of [RhCl(PPh$_3$)$_3$] (0.29 g, 0.31 mmol) and (**1c**) (0.5 g, 2.25 mmol) were heated in benzene (5 cm^3) until there was complete dissolution of the starting material. The solvent was removed *in vacuo* and the residue washed with light petroleum. Addition of methanol (10 cm^3) caused a yellow solid to precipitate out (0.11 g, 0.15 mmol, 50%). N.m.r. (CD_2Cl_2): ^{1}H (300 MHz), δ 0.94 [t, 2 H, H^1, J(H^{1}H^3) = J(H^{1}P) = 3.6], 2.23 [br d, 2 H, H^2, AA′XX′, |$J_{AX} + J_{AX'}$| 3.3], 3.10 [dd, 2 H, H^3, J(H^{3}H^1) 3.6, J(H^{3}P) 9.6], 7.55 (m, 30 H, PPh$_3$); ^{13}C-{^{1}H} (75 MHz), δ 56.7 [d, C^3, J(C^{3}Rh) 13.4], 64.42 [1:3:1:0.5:0.5:1:3:1 octet, C^2, AMXX′, J(CP) $-$26, J(CP′) 5, J(CRh) 7, J(PRh) 151, J(P′Rh) 151, J(PP′) 5], and 111.12 [dt, C^1, J(C^{1}Rh) 3.7, J(C^{1}P) 5.4]; ^{31}P-{^{1}H}, δ 28.7 p.p.m. [d, J(PRh) 151.4].

Chloro(*nitrosyl*)(η^4-*trimethylenemethane*)*triphenylphosphine*)*osmium*. [OsCl(NO)(PPh$_3$)$_3$] ($\sim$0.94 g, 0.9 mmol) and (**1c**) (0.6 g, 2.7 mmol) were stirred in benzene (20 cm^3). The green suspension dissolved after 20 min to give an orange solution. The solvent was reduced *in vacuo* to *ca.* 1 cm^3. Light petroleum (35 cm^3) was added and the suspension was filtered to give an orange solution. The solvent was removed *in vacuo* and the residue stirred with light petroleum. The crude solid obtained was chromatographed on a short alumina column. Elution with dichloromethane gave an orange band which on addition of light petroleum gave [OsCl(NO)(PPh$_3$)(η^4-tmm)] (0.1 g, 20%), m.p. 187—189 °C (decomp.) (Found: C, 46.9; H, 3.9; N, 2.1. $C_{22}H_{21}ClNOOsP$ requires C, 46.2; H, 3.7; N, 2.4%). I.r.: ν_{NO} 1 770, ν_{OsCl} 290 cm^{-1}. N.m.r. (CDCl$_3$): ^{1}H (300 MHz), δ 1.85 [dd, 1 H, H^3, J(H^{3}H^6) 5.0, J(H^{3}P) 9.4], 1.99 [d, 1 H, H^4, J(H^{4}H^1) 5.5], 2.09 [d, 1 H, H^1, J(H^{1}H^4) 5.5], 2.68 [br t, 1 H, H^2, J(H^{2}H^5) = J(H^{2}P) = 3.0], 3.26 [t, 1 H, H^6, J(H^{6}H^3) = J(H^{6}P) 5.0], 3.61 [t, 1 H, H^5, J(H^{5}H^2) = J(H^{5}P) = 3.0], and 7.5 (m, 15 H, PPh$_3$); ^{13}C-{^{1}H} (75 MHz), δ 46.3 (s, C^3 or C^4), 60.15 [d, C^2, J(C^{2}P) 27.6], 66.98 (s, C^3 or C^4), and 114.6 p.p.m. (s, C^1).



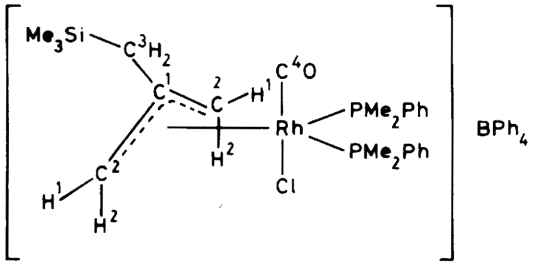
M = Os or Ru

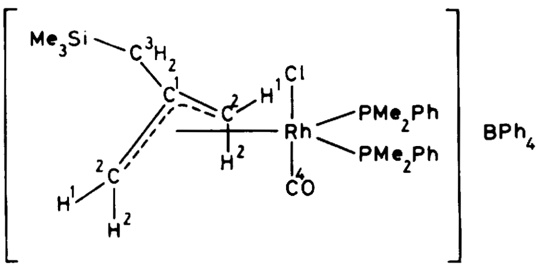
X = NO, Y = Cl or X = Cl, Y = NO

(exact position of X and Y not determined)

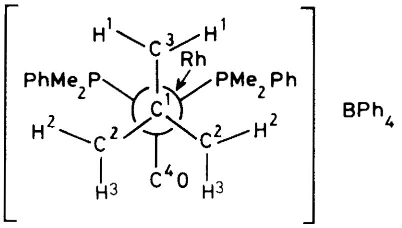
Chloro(*nitrosyl*)(η^4-*trimethylenemethane*)(*triphenylphosphine*)*ruthenium*. [RuCl$_3$(NO)(PPh$_3$)$_2$] (0.6 g, 0.585 mmol) suspended in benzene was reduced using a Zn–Cu couple. The solution containing [RuCl(NO)(PPh$_3$)$_2$] (0.585 mmol) was filtered and (**1c**) (0.39 g, 1.75 mmol) was added. The green colour gradually disappeared. After stirring for 14 h the solvent was removed *in vacuo*. The residue was washed with light petroleum (40 cm^3) and diethyl ether (30 cm^3), and chromatographed on an alumina column. Elution with dichloromethane produced an orange band which on addition of light petroleum gave the title complex (0.06 g, 20%), m.p. 129 °C (decomp.) (Found: C, 54.2; H, 4.4; N, 2.9. $C_{22}H_{21}ClNOPRu$ requires C, 54.7; H, 4.4; N, 2.9%). I.r.: ν_{NO} 1 775, ν_{RuCl} 280 cm^{-1}. N.m.r. (CD_2Cl_2): ^1H (400 MHz), δ 2.13 [d, 1 H, H^1, $J(H^1H^4)$ 5.2], 2.18 [t, 1 H, H^2, $J(H^2H^5) = J(H^2P) = 3.5$], 2.34 [dd, 1 H, H^3, $J(H^3H^6)$ 4.4, $J(H^3P)$ 9.2], 2.49 [d, 1 H, H^4, $J(H^4H^1)$ 5.2], 3.38 [dd, 1 H, H^6, $J(H^6H^3)$ 4.4, $J(H^6P)$ 6.72], 3.44 [dd, 1 H, H^5, $J(H^5H^2)$ 3.5, $J(H^5P)$ 5.1], and 7.5 (m, 15 H, PPh_3); ^{13}C-{^1H} (100 MHz), 58.98 (s, C^3 or C^4), 67.48 [d, C^2, $J(C^2P)$ 28.8], 77.28 (s, C^3 or C^4), and 117.87 p.p.m. (s, C^1).

Preparation of [Rh{η^3-$CH_2C(CH_2SiMe_3)CH_2$}Cl(CO)-($PMe_2Ph)_2$]BPh_4 (**6**). Compound (**1c**) (0.75 g, 3.38 mmol) was added to a stirred suspension of *trans*-[RhCl(CO)($PMe_2Ph)_2$] (0.5 g, 1.14 mmol) in methanol (5 cm^3). The suspension immediately dissolved leaving a dark brown-red solution. $NaBPh_4$ (0.396 g, 1.16 mmol) in methanol (2 cm^3) was added and immediately a yellow precipitate formed which was filtered off and washed with water (3 cm^3), methanol (2 cm^3), and diethyl ether (2 cm^3). Yield: 0.81 g (0.91 mmol, 80%), 114—115 °C (Found: C, 64.8; H, 6.4. $C_{48}H_{57}BClOP_2RhSi$ requires C, 65.3; H, 6.5%). I.r.: ν_{CO} 2 070 cm^{-1}. N.m.r. (CD_2Cl_2): ^1H (400 MHz), δ 0.38 (s, 9 H, $SiMe_3$), 1.80 [d, 6 H, P*Me*$_2$Ph, $|^2J(PH) + {}^4J(PH)|$ 11.27], 1.86 [br s, 2 H, CH_2SiMe_3; other isomer 1.88 (br s)], 1.88 [d, 6 H, P*Me*$_2$Ph, $|^2J(PH) + {}^4J(PH)|$ 7.33], 3.52 {d, 2 H, H^2, $J(H^2P)$ 9.45; other isomer 3.53 [d, $J(H^2P)$ 9.05]}, 4.12 {d, 2 H, H^1, $J(H^1P)$ 3.39; other isomer 4.19 [d, $J(H^1P)$ 3.76]}, 7.13 (m, 10 H, PMe_2*Ph*), and 7.6 (m, 20 H, BPh_4); ^{13}C-{^1H} (100 MHz), δ 2.13 (s, $SiMe_3$), 13.97 {d, second order, Me, PMe_2Ph, $|^1J(PC) + {}^3J(PC)|$35.56; other isomer 14.1 [d, second order, Me, PMe_2Ph, $|^1J(PC) + {}^3J(PC)$ 36.54]}, 17.02 {d, second order, Me, PMe_2Ph, $|^1J(PC) + {}^3J(PC)|$ 35.5; other isomer 17.05 [d, second order, Me, PMe_2Ph, $|^1J(PC) + {}^3J(PC)|$ 36.3]}, 31.94 [s, C^3; other isomer 24.6 (s)], 69.3 [m, C^2, AMXX′ system; other isomer 73.45 (m, AMXX′ system)], 145.29 (m, C^1), and 182.7 p.p.m. [d t, C^4, $J(C^4Rh)$ 62.3, $J(C^4P)$ 10.12]; ^{31}P-{^1H} (162 MHz), δ −2.48 {d, J(PRh) 101; other isomer −2.15 [d, J(PRh) 102.1}. The complex exists as two isomers in a ratio of 3:1 (see below).





Carbonylbis(dimethylphenylphosphine)(η^4-trimethylenemethane)rhodium tetraphenylborate (**9**). Sodium fluoride (0.06 g, 1.4 mmol) was added to a solution of complex (**6**) (0.05 g, 0.056 mmol) in aqueous methyl cyanide (5 cm^3). After standing for 12 h at room temperature the solvent was removed *in vacuo* and the residue extracted with dichloromethane (15 cm^3) and dried over anhydrous potassium carbonate. The solvent was removed *in vacuo* and ^1H and ^{31}P n.m.r. spectra showed complete reaction. Recrystallisation from dichloromethane–diethyl ether afforded pale yellow needles (0.035 g, 0.045 mmol, 80% recovered), m.p. 108—109°C (Found: C, 68.7; H, 6.2. $C_{45}H_{48}BOP_2Rh$ requires C, 69.2; H, 6.2%). I.r.: ν_{CO} 2 058 cm^{-1}; n.m.r. ($CDCl_3$): ^1H (300 MHz), δ 1.22 [m, second order, 6 H, P*Me*$_2$Ph, $|^2J(PH) + {}^4J(PH)|$ 8.84], 1.32 [m, second order, 6 H, P*Me*$_2$Ph, $|^2J(PH) + {}^4J(PH)|$ 8.5], 1.86 [br d, 2 H, second order AA′XX′, H^2, $|J(H^2P) + J(H^2P')|$ 1.6], 2.13 [dd, 2 H, H^1, $J(H^1H^3)$ 4.2, $J(H^1P)$ 6.3], 2.65 [dd, 2 H, H^3, $J(H^3H^1)$ 4.2, $J(H^3P)$ 6.7], and 7.5 (m, 30 H, PMe_2*Ph* and BPh_4); ^{13}C-{^1H} (75 MHz), δ 17.0—19.0 (m, P*Me*$_2$Ph, AMXX′ system), 60.6 [1:1:3:3:3:3:3:3:1:1, dectet, AMXX′, C^2, J(CP) −28, J(CP′) 5, J(CRh) 5.7, J(PRh) 132, J(P′Rh) 132, J(PP′) 17], 62.7 [d, C^3, $J(C^3Rh)$ 7.5], 112.3 [dt, C^1, $J(C^1Rh)$ 3.3, $J(C^1P)$ 5.0], and 190.0 p.p.m. [dt, C^4, $J(C^4Rh)$ 63.3, $J(C^4P)$ 10.7]; ^{31}P-{^1H}, δ 4.134 p.p.m. [d, J(PRh) 131.8].



Reaction of trans-[IrCl(CO)($PMe_2Ph)_2$] *with* (**1c**).—(**1c**) (0.63 g, 2.81 mmol) was added to a stirred solution of *trans*-[IrCl(CO)($PMe_2Ph)_2$] (0.5 g, 0.94 mmol) in methanol (7 cm^3). After 2 min $NaBPh_4$ (0.35 g, 1.02 mmol) in methanol (5 cm^3) was added to the pale yellow solution. The white precipitate was filtered off and washed with methanol (10 cm^3) and dried *in vacuo*. Yield: 0.6 g (0.66 mmol, 70%), m.p. 168—170 °C (decomp.). I.r.: ν_{CO} 2 050 cm^{-1}. N.m.r. (CD_2Cl_2): ^1H (90 MHz), δ 1.7 [d, P*Me*$_2$Ph, $|^2J(PH) + {}^4J(PH)|$ 10.5], 1.85 [d, P*Me*$_2$Ph, $|^2J(PH) + {}^4J(PH)|$ 10.5], 10.5], 2.2 (s, 3 H, CH_3), 3.0 [d, 2 H, CH_2 (*anti*), J(HP) 6.8], 3.8 [br s, 2 H, CH_2 (*syn*)], and 7.5 (m, 30 H, BPh_4 and PMe_2*Ph*).

The hydrogen-1 n.m.r. is identical to that of [Ir{η^3-CH_2C-(Me)CH_2}Cl(CO)($PMe_2Ph)_2$]BPh_4.[13]

Reaction of [RhH(CO)($PPh_3)_3$] *with* (**1c**).—To a solution of [RhH(CO)($PPh_3)_3$] (0.4 g, 0.44 mmol) in toluene (15 cm^3) was added (**1c**) (0.3 g, 1.35 mmol). A yellow solid was precipitated and after 0.5 h the solution was filtered and the product washed with light petroleum to give *trans*-[Rh{OS(O)$_2$Me}(CO)-($PPh_3)_2$] (0.28 g, 0.37 mmol, 85%), m.p. 170—172 °C (decomp.) (Found: C, 60.7; H, 4.5. $C_{38}H_{33}O_4P_2RhS$ requires C, 60.8; H, 4.4). I.r.: ν_{CO} 1 980 cm^{-1}. N.m.r. ($CDCl_3$); ^1H (90 MHz), δ 1.55 (s, 3 H, $MeSO_3$), 7.5 (m, 30 H, PPh_3); ^{31}P-{^1H} (24.15 MHz), δ 28.4 p.p.m. [d, J(PRh) 127].

Acknowledgements

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