Reactions of 3-Trimethylsilyl-2-(methylsulphonyloxymethyl)prop-1-ene with Low-valent Complexes of Molybdenum, Ruthenium, Osmium, Rhodium, Iridium, Palladium, and Platinum. New Syntheses of η^4-Trimethylenemethane Complexes of Ruthenium, Osmium, and Iridium

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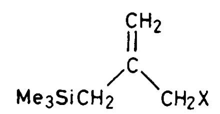
The η^4-trimethylenemethane (tmm) metal complexes [MCl(NO)(PPh$_3$)(tmm)] (M = Ru or Os), [Os(CO)$_2$(PPh$_3$)(tmm)], [IrX(CO)(L)(tmm)] (X = Cl, L = PPh$_3$ or AsPh$_3$; X = Br, L = PPh$_3$), [IrCl(PPh$_3$)$_2$(tmm)], and [Ir(CO)(PPh$_3$)$_2$(tmm)][OS(O)$_2$Me] have been prepared in good yields by the action of Me$_3$SiCH$_2$C(=CH$_2$)-{CH$_2$OS(O)$_2$Me} upon [MCl(NO)(PPh$_3$)$_n$] (M = Ru, n = 2; M = Os, n = 3), [IrX(CO)L$_2$], [Ir$_2$Cl$_2$(C$_8$H$_{14}$)$_4$] + 4PPh$_3$, and [IrH(CO)(PPh$_3$)$_3$].

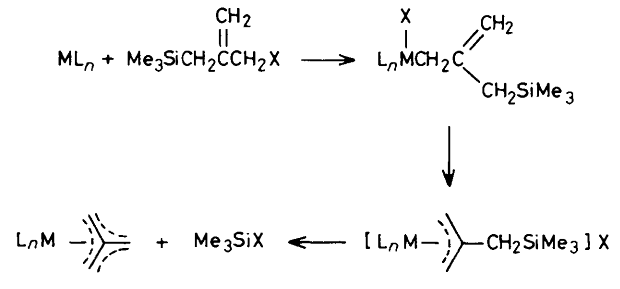
The importance of a trimethylenemethane–palladium complex in the palladium-mediated cycloaddition approach to cyclopentanoids[1] has caused us to investigate the synthesis and chemistry of trimethylenemethane metal complexes. Thus using the reagents (**1a**) and (**1b**), introduced by Trost[1] to synthesise a trimethylenemethane–palladium complex, we have been able to obtain the osmium and iridium complexes [Os(CO)$_2$(PPh$_3$)(tmm)] and [IrCl(CO)(PPh$_3$)(tmm)] (tmm = η^4-trimethylenemethane) by reaction of (**1a**) or (**1b**) with [Os(CO)$_2$(PPh$_3$)$_3$] or *trans*-[IrCl(CO)(PPh$_3$)$_2$].[2] However, the yields of the tmm complexes are low and further studies on their chemical reactivity are inhibited. Following the pathway proposed for the formation of the reactive intermediate [Pd(η^3-tmm)(PPh$_3$)$_2$],[1] a plausible route to the tmm complexes of osmium and iridium may involve oxidative-addition of the allylic compounds (**1a**) or (**1b**) to a co-ordinatively unsaturated metal species to give an η^1-allyl, formation of an η^3-allyl, and elimination of Me$_3$SiX as outlined in Scheme 1. A key step in this mechanism is the ionisation of a silylophile X from the metal centre followed by attack at silicon by X resulting in desilylation of the η^3-trimethylsilylallyl intermediate. The ability of allylic methanesulphonates to add rapidly and oxidatively to iridium(I) centres coupled with the poor co-ordinating ability of the methanesulphonate group[3] suggested that the methanesulphonate (**1c**)[4] might be an attractive precursor to tmm metal complexes. In this communication we describe reactions of the methanesulphonate (**1c**) with a variety of low-valent metal complexes which lead to much improved yields of η^4-trimethylenemethane metal complexes.

In a typical experiment treatment of *trans*-[IrCl(CO)(PPh$_3$)$_2$] with (**1c**)[4] in refluxing toluene affords [IrCl(CO)(PPh$_3$)(tmm)] in 75% yield. In contrast using the

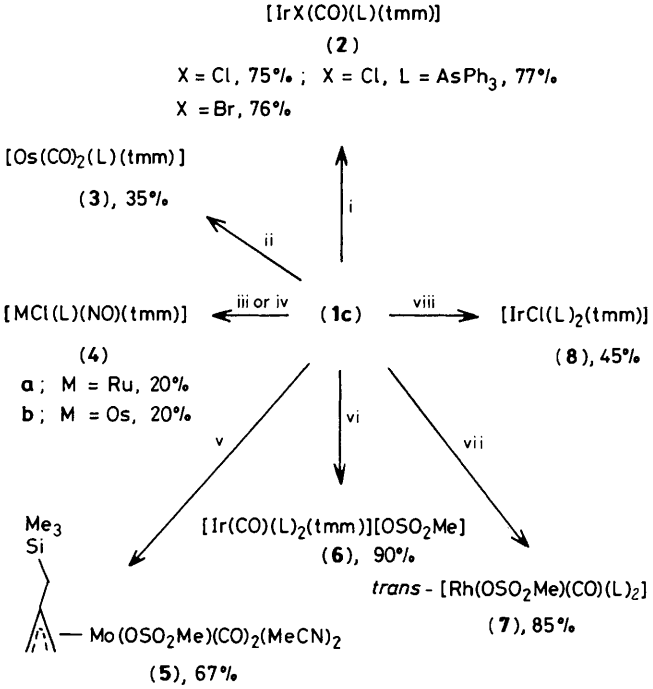


(1)

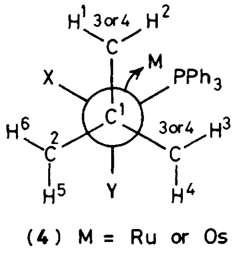
a; X = OAc
b; X = Cl
c; X = OS(O)$_2$Me



Scheme 1



Scheme 2. L = PPh$_3$. *Reagents:* i, *trans*-[IrX(CO)(L)$_2$]; ii, [Os(CO)$_2$(L)$_3$]; iii, [RuCl(NO)(L)$_2$]; iv, [OsCl(NO)(L)$_3$]; v, Mo(CO)$_6$, MeCN; vi, [IrH(CO)(L)$_3$]; vii, [RhH(CO)(L)$_3$]; viii, [Ir$_2$Cl$_2$(cyclo-octene)$_4$] + 4 L.

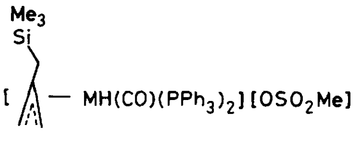


(**4**) M = Ru or Os

The relative positions of the nitrosyl and chlorine ligands have not been established. Either X = NO, Y = Cl or X = Cl, Y = NO.

chloride (**1b**) the yield is 11% and about 50% of *trans*-$[IrCl(CO)(PPh_3)_2]$ is recovered unchanged.[2] Other reactions of (**1c**) with a variety of low-valent metal complexes are outlined in Scheme 2. The η^4-trimethylenemethane complexes have been characterised on the basis of microanalytical data and their spectroscopic properties,[†] the trimethylenemethane ligand adopting the usual umbrella arrangement about the metal atom. The isolation of $[RuCl(NO)(PPh_3)(tmm)]$ (**4a**) provides the first reported example of a trimethylenemethane complex of ruthenium. The analogous osmium complex (**4b**) can also be obtained (Scheme 2) and these two complexes are the first examples of nitrosyl trimethylenemethane metal complexes.

The formation of the tmm complexes (**2**)—(**4**) can readily be accounted for in terms of the mechanism outlined in Scheme 1. Interestingly the attempted preparation of an η^4-trimethylenemethane complex of molybdenum by reaction of (**1c**) with $[Mo(CO)_6]$ in a mixture of methyl cyanide and benzene failed and the η^3-trimethylsilylmethylallyl complex (**5**) was isolated in high yield. The lack of desilylation of molybdenum η^3-allyls as compared to palladium η^3-allyls has been noted previously[5] and the isolation of (**5**) provides a further example of the stability of trimethylsilylmethylallyls of molybdenum. In the absence of silylophilic reagents we have been able to isolate in high yield the trimethylsilylmethylallyl complexes of palladium and platinum $[M\{\eta^3\text{-}CH_2C(CH_2SiMe_3)CH_2\}(PPh_3)_2][PF_6]$ (M = Pd or Pt) by the action of (**1c**) upon $[Pd(PPh_3)_4]$ or $[Pt(C_2H_4)(PPh_3)_2]$ in the presence of NH_4PF_6.



(**9**)

The isolation of the palladium complex is of interest since it is one of the intermediates implicated in the generation of the catalyst $[Pd(\eta^3\text{-}tmm)(PPh_3)_2]$.[1]

Treatment of $[IrH(CO)(PPh_3)_3]$ with (**1c**) affords the trimethylenemethane complex (**6**) in 90% yield providing a good route to a rare example of a cationic trimethylenemethane metal complex.[6] Elimination of trimethylsilane from an intermediate of the type (**9**, M = Ir) provides an attractive pathway to this trimethylenemethane–iridium complex. An attempt to obtain the rhodium analogue of (**6**) by reaction of $[RhH(CO)(PPh_3)_3]$ with (**1c**) gave only the complex *trans*-$[Rh\{OS(O)_2Me\}(CO)(PPh_3)_2]$ (**7**) in 85% yield. In this reaction reductive elimination of $Me_3SiCH_2C(Me){=}CH_2$ is presumably faster than either elimination of trimethylsilane or desilylation of the η^3-trimethylsilylmethylallyl intermediate (**9**, M = Rh).

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[†] Selected spectroscopic data (coupling constants in Hz). Compound (**4a**), i.r. (CsCl disc): ν_{NO} 1775, ν_{RuCl} 280 cm^{-1}; n.m.r. (CD_2Cl_2): ^1H (400 MHz), δ 2.13 [d, 1H, H^1, $J(H^1H^4)$ 5.2], 2.18 [t, 1H, H^2, $J(H^2H^5) = J(H^2P) = 3.5$], 2.34 [dd, 1H, H^3, $J(H^3H^6)$ 4.4, $J(H^3P)$ 9.2], 2.49 [d, 1H, H^4, $J(H^4H^1)$ 5.2], 3.38 [dd, 1H, H^6, $J(H^6H^3)$ 4.4, $J(H^6P)$ 6.72], and 3.44 [dd, 1H, H^5, $J(H^5H^2)$ 3.5, $J(H^5P)$ 5.1]; $^{13}C\text{-}\{^1H\}$(100 MHz), δ 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 117.27 (s, C^1). Compound (**4b**), i.r. (CsCl disc): ν_{NO} 1770, ν_{OsCl} 290 cm^{-1}; n.m.r. ($CDCl_3$): ^1H(300 MHz), δ 1.85 [dd, 1H, H^3, $J(H^3H^6)$5.0, $J(H^3P)$ 9.4], 1.99 [d, 1H, H^4, $J(H^4H^1)$ 5.5], 2.09 [d, 1H, H^1, $J(H^1H^4)$ 5.5], 2.68 [br.t, 1H, H^2, $J(H^2H^5) = J(H^2P) = 3.0$], 3.26 [t, 1H, H^6, $J(H^6H^3) = J(H^6P) = 5.0$], and 3.61 [t, 1H, H^5, $J(H^5H^2) = J(H^5P) = 3.0$]; $^{13}C\text{-}\{^1H\}$(75 MHz), δ 46.3 (s, C^3 or C^4), 60.15 [d, C^2, $J(C^2P)$ 27.6], 66.98 (s, C^3 or C^4), and 114.6 (s, C^1).