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Preliminary communication

SELENOCARBONYL COMPLEXES OF IRIDIUM(I) AND IRIDIUM(III). SYNTHESIS AND REACTIONS OF $IrCl(CSe)(PPh_3)_2$

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Summary

A five-step conversion of $IrCl(CO)(PPh_3)_2$ into $IrCl(CSe)(PPh_3)_2$ via $Ir(\eta^2\text{-}CSe_2)Cl(CO)(PPh_3)_2$ is described. $IrCl(CSe)(PPh_3)_2$ is oxidized by Cl_2 to $IrCl_3(CSe)(PPh_3)_2$ and by O_2 to $Ir(\eta^2\text{-}O_2)Cl(CSe)(PPh_3)_2$, and reaction with Ag^+ in MeCN gives $[Ir(CSe)(MeCN)(PPh_3)_2]^+$. $NaBH_4$ in the presence of PPh_3 reduces $IrCl(CSe)(PPh_3)_2$ completely to $IrH_2(SeMe)(PPh_3)_3$ and the η^2-CSe_2 adduct, $Ir(\eta^2\text{-}CSe_2)Cl(CSe)(PPh_3)_2$, with MeI forms the metallacycle $[\overline{\mathrm{Ir(C[SeMe]SeC}}\mathrm{[SeMe])I_2(PPh_3)_2]^+}$.

Interesting discoveries have followed the study of transition metal thiocarbonyl complexes. These include (i) the alkylation of S in low valent CS complexes which constitutes an important route to thiocarbyne complexes [1], (ii) the involvement of CS in migratory-insertion reactions which has led to thioacyl groups [2] and for the special case of hydride migration, to thioformyl and thence to formyl ligands [3], (iii) the formation of unsaturated metallacycles, e.g. "metallabenzenes" [4] and "metallacyclobutadienes" [5]. Similar chemistry must await discovery for selenocarbonyl complexes but the growth of this area is restricted by generally unsatisfactory synthetic routes to selenocarbonyl-containing starting materials. Presently available methods rely on modification and fragmentation of η^2-CSe_2 [6] or η^2-CSeS [7] and substitution reactions of CCl_2 complexes [8,9]. An obvious synthetic target is $IrCl(CSe)(PPh_3)_2$ especially in view of the important role $IrCl(CO)(PPh_3)_2$ has played in organometallic chemistry and the fact that $IrCl(CS)(PPh_3)_2$ was one of the first thiocarbonyl complexes to be described. As a first step in the examination of the selenocarbonyl chemistry of iridium we describe here a straightforward five-step conversion of $IrCl(CO)(PPh_3)_2$ to $IrCl(CSe)(PPh_3)_2$ and some further simple reactions of this new complex.

The preparation of $IrCl(CSe)(PPh_3)_2$ follows the steps outlined in Scheme 1.

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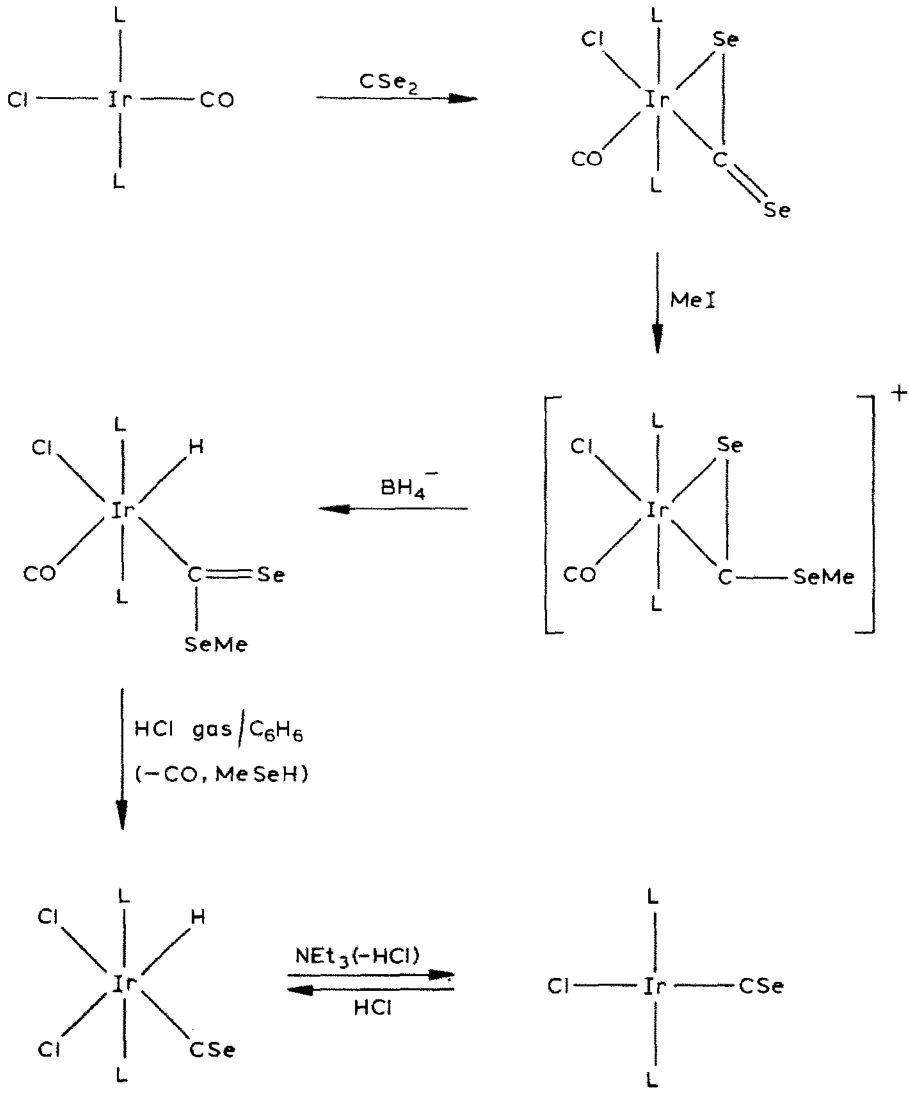


SCHEME 1. Conversion of IrCl(CO)(PPh$_3$)$_2$ to IrCl(CSe)(PPh$_3$)$_2$ (L = PPh$_3$).

The η^2-CSe$_2$ adduct has been described previously [10]. Methylation with MeI yields the η^2-diselenomethylester complex which is readily converted to a η^1-CSe$_2$Me complex by the introduction of hydride ligand using NaBH$_4$. The synthesis so far parallels that already described for IrCl(CS)(PPh$_3$)$_2$ [11] but Ir(η^1-CSe$_2$Me)HCl(CO)(PPh$_3$)$_2$ does not eliminate MeSeH thermally. However, anhydrous HCl gas in benzene solution does cleave MeSeH and form IrHCl$_2$(CSe)(PPh$_3$)$_2$. This colourless material is easily dehydrohalogenated with a base like triethylamine to IrCl(CSe)(PPh$_3$)$_2$ which forms orange, needle-like crystals, m.p. 247—249°C. There is a strong IR absorption at 1198 cm^{-1} which must be associated largely with C—Se stretching. ν(CSe)

TABLE 1

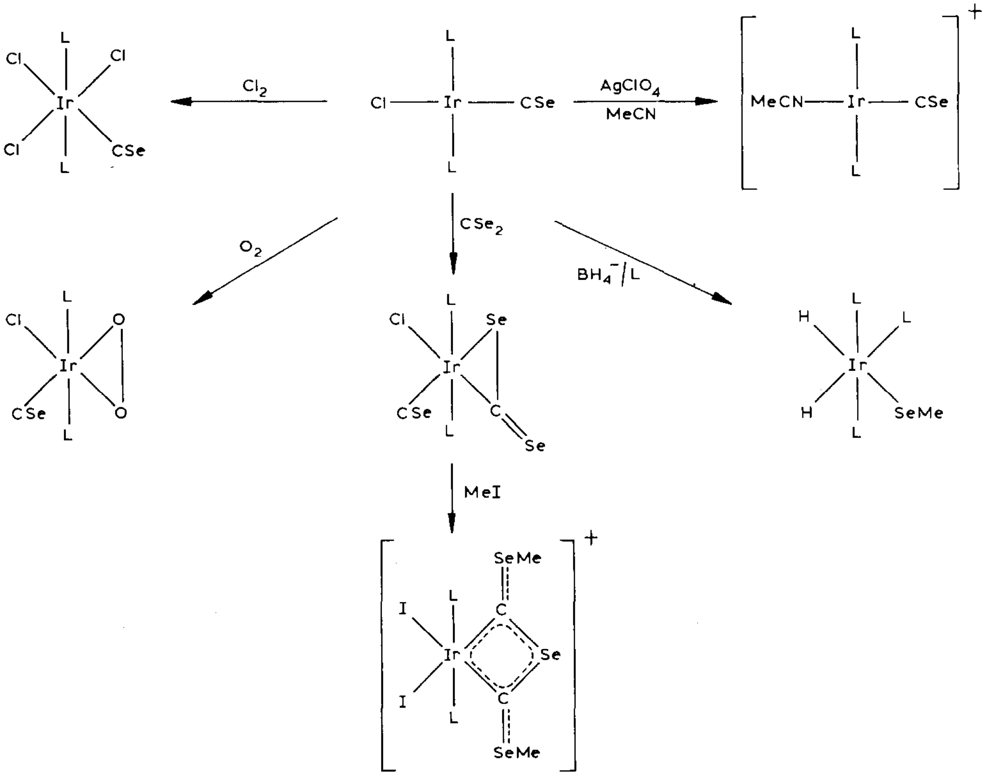
IR DATA [a] FOR IRIDIUM SELENOCARBONYL COMPLEXES

Compound [b]	ν(CSe)	Other bands
$Ir(\eta^2\text{-}CSe_2)Cl(CO)(PPh_3)_2$	1005, 995	2025, 2000, 1990, ν(CO)
$[Ir(\eta^2\text{-}CSe_2Me)Cl(CO)(PPh_3)_2)ClO4$	1000	2045, ν(CO)
$Ir(\eta^2\text{-}CSe_2Me)HCl(CO)(PPh_3)_2$	860	2045, ν(CO); 2000, ν(IrH)
$IrCl(CSe)(PPh_3)_2$	1198	
$IrHCl_2(CSe)(PPh_3)_2$	1200	2240, ν(IrH)
$IrCl_3(CSe)(PPh_3)_2$	1201	
$[Ir(CSe)(MeCN)(PPh_3)_2]ClO_4$	1184	2320, ν(CN)
$[Ir(CSe)(CO)_2(PPh_3)_2]ClO_4$	1145	2060, 2000, ν(CO)
$IrH_2(SeMe)(PPh_3)_3$		2130, 2050, ν(IrH)
$Ir(O_2)Cl(CSe)(PPh_3)_2$	1165	848, $\nu(O_2)$
$Ir(\eta^2\text{-}CSe_2)Cl(CSe)(PPh_3)_2$	1175, 1010	
$[\overline{Ir(C[SeMe]SeC}[SeMe])I_2(PPh_3)_2]ClO_4$	863	

[a] cm^{-1} measured as Nujol mulls. [b] All compounds have satisfactory elemental analyses.

bands for other selenocarbonyl complexes reported here are collected in Table 1.

Like $IrCl(CO)(PPh_3)_2$, $IrCl(CSe)(PPh_3)_2$ is readily oxidised by Cl_2 to $IrCl_3(CSe)(PPh_3)_2$, with oxygen forms a dioxygen adduct $Ir(O_2)Cl(CSe)(PPh_3)_2$, and with $AgClO_4$ in acetonitrile forms $[Ir(CSe)(MeCN)(PPh_3)_2]ClO_4$. From

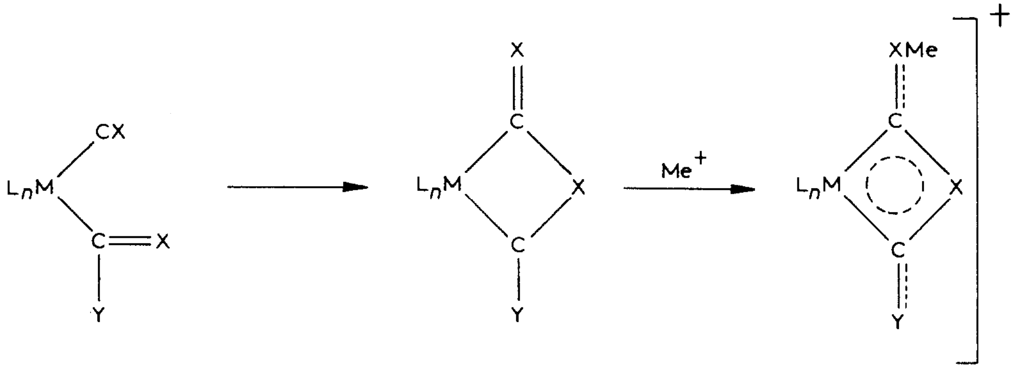


SCHEME 2. Reactions of $IrCl(CSe)(PPh_3)_2$ ($L = PPh_3$).

this cation other cations, e.g. $[Ir(CSe)(CO)_2(PPh_3)_2]^+$ can be readily derived. Unlike $IrCl(CO)(PPh_3)_2$, however, it should be noted that $\nu(CSe)$ values for these adducts (see Table 1) do not necessarily rise upon oxidation or conversion to a cation. In fact the dioxygen adduct has $\nu(CSe)$ lowered by 33 cm^{-1} from $IrCl(CSe)(PPh_3)_2$. This must reflect extensive mixing of $\nu(CSe)$ modes with lower energy modes particularly $\nu[Ir{-}(CSe)]$. $\nu(CSe)$ is not, therefore, a useful measure of metal electron density in the way in which $\nu(CO)$ is so useful.

Reaction of $IrCl(CSe)(PPh_3)_2$ (Scheme 2) with $NaBH_4$ in the presence of PPh_3, which in the case of $IrCl(CO)(PPh_3)_2$ and $IrCl(CS)(PPh_3)_2$ leads to $IrH(CO)(PPh_3)_3$ and $IrH(CS)(PPh_3)_3$, respectively, leads here instead to complete reduction of the selenocarbonyl ligand and the final product is $IrH_2(SeMe)(PPh_3)_3$. This reduction must proceed via selenoformaldehyde-coordinated intermediates. Osmium selenoformaldehyde complexes are now known [12].

CSe_2 reacts with $IrCl(CSe)(PPh_3)_2$ to form the adduct $Ir(\eta^2\text{-}CSe_2)Cl(CSe)(PPh_3)_2$. Methylation of the η^2-CSe_2 in this molecule with MeI giving $[Ir(\eta^2\text{-}CSe_2Me)Cl(CSe)(PPh_3)_2]^+$, is followed by immediate condensation between the diselenomethyl-ester ligand and CSe and further methylation at Se forms the novel metallacycle $[\overline{Ir(C[SeMe]SeC}[SeMe])I_2(PPh_3)_2]^+$. Similar condensations occur between thiocarboxamide and thiocarbonyl ligands and the cyclic ligand resulting in this case has been structurally characterised [13]. The general reaction may be written:



(X = S, Se, Y = NR_2, SMe, SeMe, etc.)

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