

Preliminary communication

SELENOCARBONYL COMPLEXES OF IRIDIUM(I) AND IRIDIUM(III). SYNTHESIS AND REACTIONS OF $\text{IrCl}(\text{CSe})(\text{PPh}_3)_2$

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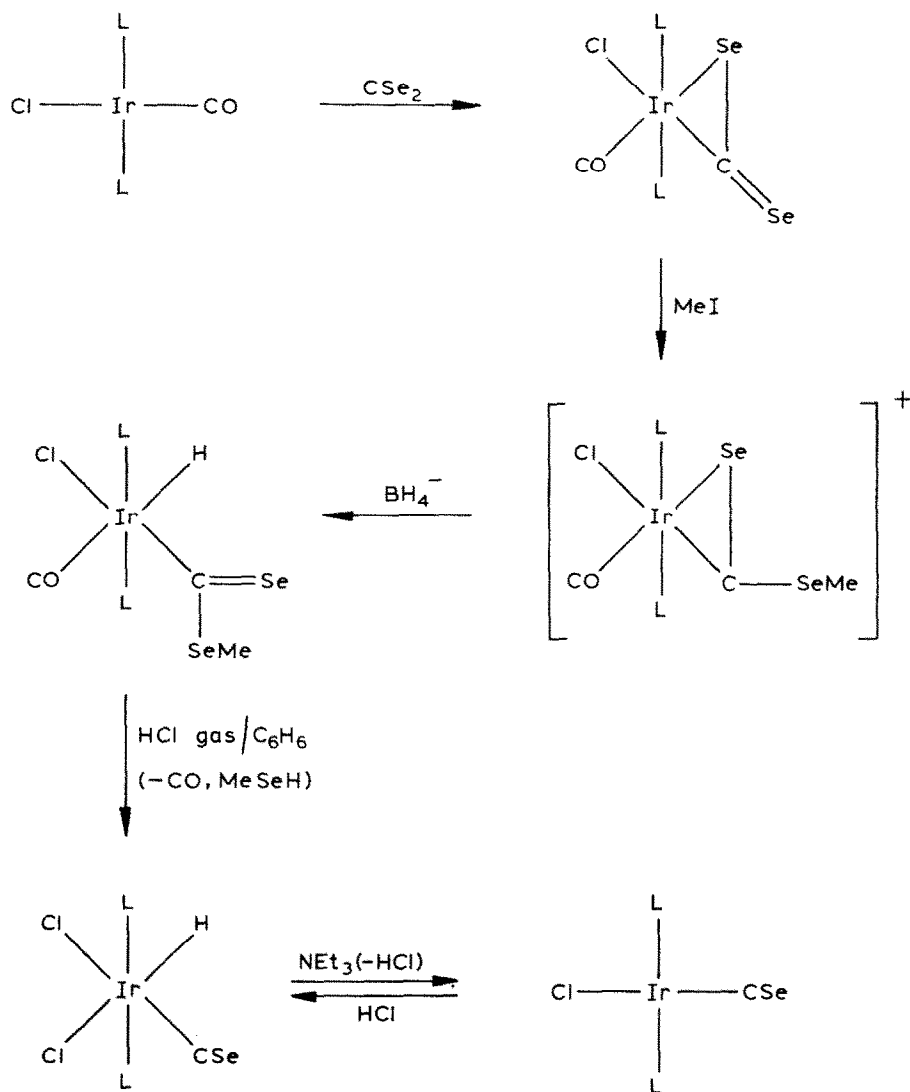
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Summary

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

Interesting discoveries have followed the study of transition metal thio-carbonyl complexes. These include (i) the alkylation of S in low valent CS complexes which constitutes an important route to thiocarbonyne 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 $\eta^2\text{-CSe}_2$ [6] or $\eta^2\text{-CSeS}$ [7] and substitution reactions of CCl_2 complexes [8,9]. An obvious synthetic target is $\text{IrCl}(\text{CSe})(\text{PPh}_3)_2$ especially in view of the important role $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ has played in organometallic chemistry and the fact that $\text{IrCl}(\text{CS})(\text{PPh}_3)_2$ 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 $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ to $\text{IrCl}(\text{CSe})(\text{PPh}_3)_2$ and some further simple reactions of this new complex.

The preparation of $\text{IrCl}(\text{CSe})(\text{PPh}_3)_2$ follows the steps outlined in Scheme 1.



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

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_2Me complex by the introduction of hydride ligand using NaBH_4 . The synthesis so far parallels that already described for $\text{IrCl(CS)(PPh}_3)_2$ [11] but $\text{Ir}(\eta^1\text{-CSe}_2\text{Me})\text{HCl(CO)(PPh}_3)_2$ does not eliminate MeSeH thermally. However, anhydrous HCl gas in benzene solution does cleave MeSeH and form $\text{IrHCl}_2(\text{CSe})(\text{PPh}_3)_2$. This colourless material is easily dehydrohalogenated with a base like triethylamine to $\text{IrCl(CSe)(PPh}_3)_2$ which forms orange, needle-like crystals, m.p. $247\text{--}249^\circ\text{C}$. There is a strong IR absorption at 1198 cm^{-1} which must be associated largely with C-Se stretching. $\nu(\text{CSe})$

TABLE 1

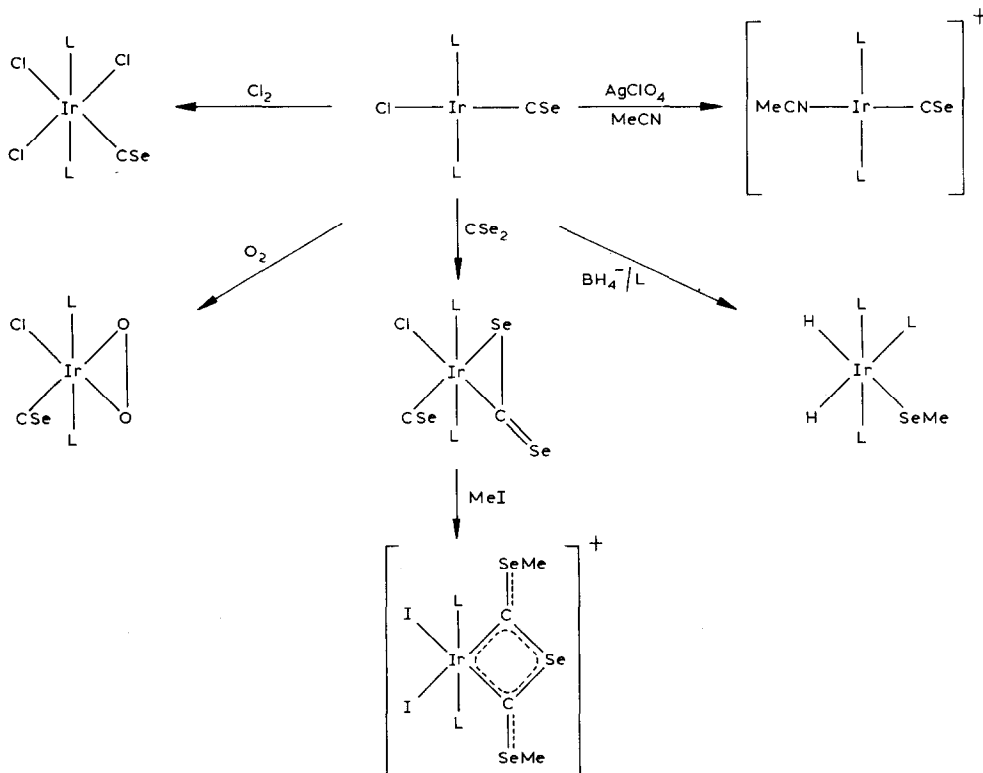
IR DATA ^a FOR IRIUM SELENOCARBONYL COMPLEXES

Compound ^b	$\nu(\text{CSe})$	Other bands
$\text{Ir}(\eta^2\text{-CSe}_2)\text{Cl}(\text{CO})(\text{PPh}_3)_2$	1005, 995	2025, 2000, 1990, $\nu(\text{CO})$
$[\text{Ir}(\eta^2\text{-CSe}_2\text{Me})\text{Cl}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$	1000	2045, $\nu(\text{CO})$
$\text{Ir}(\eta^2\text{-CSe}_2\text{Me})\text{HCl}(\text{CO})(\text{PPh}_3)_2$	860	2045, $\nu(\text{CO})$; 2000, $\nu(\text{IrH})$
$\text{IrCl}(\text{CSe})(\text{PPh}_3)_2$	1198	
$\text{IrHCl}_2(\text{CSe})(\text{PPh}_3)_2$	1200	2240, $\nu(\text{IrH})$
$\text{IrCl}_3(\text{CSe})(\text{PPh}_3)_2$	1201	
$[\text{Ir}(\text{CSe})(\text{MeCN})(\text{PPh}_3)_2]\text{ClO}_4$	1184	2320, $\nu(\text{CN})$
$[\text{Ir}(\text{CSe})(\text{CO})_2(\text{PPh}_3)_2]\text{ClO}_4$	1145	2060, 2000, $\nu(\text{CO})$
$\text{IrH}_2(\text{SeMe})(\text{PPh}_3)_3$		2130, 2050, $\nu(\text{IrH})$
$\text{Ir}(\text{O}_2)\text{Cl}(\text{CSe})(\text{PPh}_3)_2$	1165	848, $\nu(\text{O}_2)$
$\text{Ir}(\eta^2\text{-CSe}_2)\text{Cl}(\text{CSe})(\text{PPh}_3)_2$	1175, 1010	
$[\text{Ir}[\text{C}(\text{SeMe})\text{SeC}(\text{SeMe})]\text{L}_2(\text{PPh}_3)_2]\text{ClO}_4$	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 $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, $\text{IrCl}(\text{CSe})(\text{PPh}_3)_2$ is readily oxidised by Cl_2 to $\text{IrCl}_3(\text{CSe})(\text{PPh}_3)_2$, with oxygen forms a dioxygen adduct $\text{Ir}(\text{O}_2)\text{Cl}(\text{CSe})(\text{PPh}_3)_2$, and with AgClO_4 in acetonitrile forms $[\text{Ir}(\text{CSe})(\text{MeCN})(\text{PPh}_3)_2]\text{ClO}_4$. From

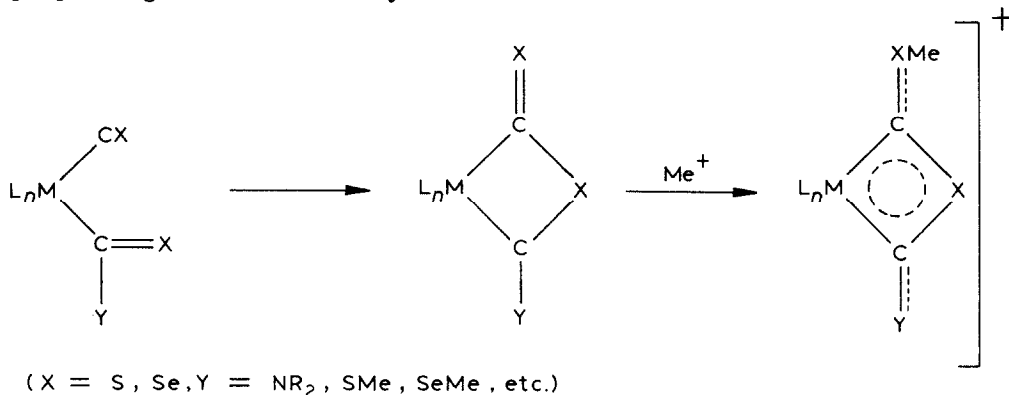


SCHEME 2. Reactions of $\text{IrCl}(\text{CSe})(\text{PPh}_3)_2$ ($\text{L} = \text{PPh}_3$).

this cation other cations, e.g. $[\text{Ir}(\text{CSe})(\text{CO})_2(\text{PPh}_3)_2]^+$ can be readily derived. Unlike $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$, however, it should be noted that $\nu(\text{CSe})$ values for these adducts (see Table 1) do not necessarily rise upon oxidation or conversion to a cation. In fact the dioxygen adduct has $\nu(\text{CSe})$ lowered by 33 cm^{-1} from $\text{IrCl}(\text{CSe})(\text{PPh}_3)_2$. This must reflect extensive mixing of $\nu(\text{CSe})$ modes with lower energy modes particularly $\nu[\text{Ir}-(\text{CSe})]$. $\nu(\text{CSe})$ is not, therefore, a useful measure of metal electron density in the way in which $\nu(\text{CO})$ is so useful.

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

CSe_2 reacts with $\text{IrCl}(\text{CSe})(\text{PPh}_3)_2$ to form the adduct $\text{Ir}(\eta^2\text{-CSe}_2)\text{Cl}(\text{CSe})(\text{PPh}_3)_2$. Methylation of the $\eta^2\text{-CSe}_2$ in this molecule with MeI giving $[\text{Ir}(\eta^2\text{-CSe}_2\text{Me})\text{Cl}(\text{CSe})(\text{PPh}_3)_2]^+$, is followed by immediate condensation between the diselenomethyl-ester ligand and CSe and further methylation at Se forms the novel metallacycle $[\text{Ir}(\text{C}[\text{SeMe}]\text{SeC}[\text{SeMe}])\text{I}_2(\text{PPh}_3)_2]^+$. 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:



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