

Synthesis and Properties of Mononuclear and Polynuclear Indenyl Iridium Complexes

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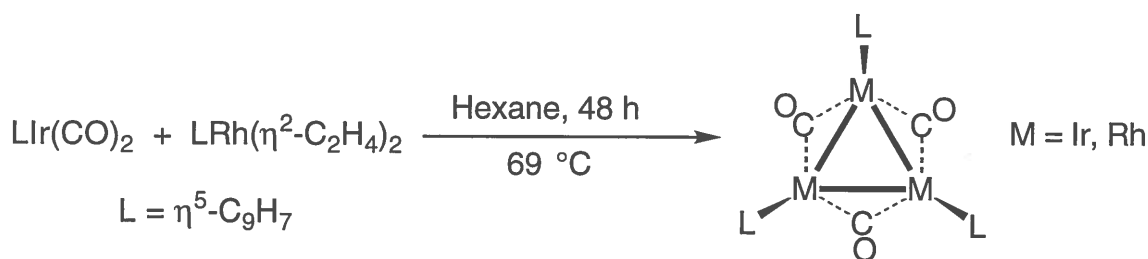
Final Seminar

August 22, 1996

Transition metal indenyl complexes generally show enhanced reactivity in associative substitution reactions compared to their cyclopentadienyl analogs, and this phenomenon has been termed the 'indenyl ligand effect.'¹

Interestingly, although the indenyl ligand effect has been vigorously researched in a multitude of mononuclear systems, related studies of polynuclear systems that incorporate indenyl metal fragments have not been reported. Therefore, we were interested in the synthesis and properties of metal cluster compounds that contain indenyl iridium fragments in order to investigate the possibility of enhancing cluster reactivity.

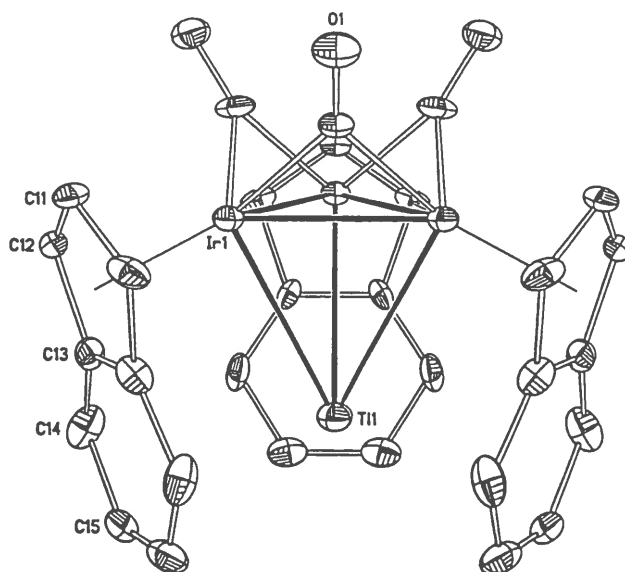
The reaction of $\text{Ir}(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)$ with $\text{Ir}(\eta^2\text{-C}_2\text{H}_4)_2(\eta^5\text{-C}_9\text{H}_7)$ provided $\text{Ir}_3(\mu\text{-CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$, and the reaction of $\text{Ir}(\text{CO})_2(\eta^5\text{-C}_9\text{H}_7)$ with $\text{Rh}(\eta^2\text{-C}_2\text{H}_4)_2(\eta^5\text{-C}_9\text{H}_7)$ provided the trinuclear clusters $\text{Ir}_{3-x}\text{Rh}_x(\mu\text{-CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$ ($x = 0 - 2$) in good yields,² as well as $\text{Rh}_3(\mu\text{-CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$ which had been studied previously.³



These compounds react readily with carbon monoxide to form mononuclear products, whereas the corresponding cyclopentadienyl compounds are much less reactive.⁴ Thus, indenyl ligand substitution does enhance the reactivity of these clusters.

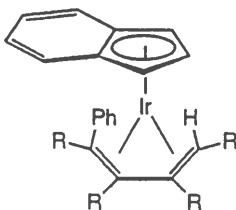
A fascinating diversity of structures has been observed for trinuclear compounds of the cobalt triad with the general formula $\text{M}_3(\text{CO})_3(\eta^5\text{-L})_3$, where L refers to $\eta^5\text{-C}_5\text{H}_5$ and related ligands.^{2, 5-7} The reaction of the triiridium cluster $\text{Ir}_3(\text{CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$ with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ gave $[\text{Ir}_3(\mu\text{-H})(\text{CO})_3(\eta^5\text{-C}_9\text{H}_7)_3][\text{BF}_4]$. Subsequent deprotonation led to generation of $\text{C}_s\text{-Ir}_3(\text{CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$, which rapidly reverted to an equilibrium mixture of major isomer $\text{C}_{3v}\text{-Ir}_3(\mu\text{-CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$ and minor isomer $\text{C}_s\text{-Ir}_3(\text{CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$. The solution dynamics and interconversion of both isomers were explored. Variable temperature ^1H and ^{13}C NMR experiments indicated that $\text{C}_s\text{-Ir}_3(\text{CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$ undergoes a dynamic process that involves the intermediacy of a third isomer of $\text{Ir}_3(\text{CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$. This study provides a unique set of relative energies in solution for three of the four observed forms for a $\text{M}_3(\text{CO})_3(\eta^5\text{-L})_3$ system.

The reactions of $\text{C}_{3v}\text{-Ir}_3(\mu\text{-CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$ with metal fragment electrophiles containing Cu, Ag, Au, and Hg provided cationic tetranuclear clusters, which show a rearrangement of the $\text{Ir}_3(\eta^5\text{-C}_9\text{H}_7)_3$ moiety to a C_s geometry. The reaction with TlPF_6 gave $[\text{Ir}_3\text{Tl}(\mu\text{-CO})_3(\eta^5\text{-C}_9\text{H}_7)_3][\text{PF}_6]$, which maintains the C_{3v} geometry of $\text{C}_{3v}\text{-Ir}_3(\mu\text{-CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$ and has the thallium ion encapsulated by the six-membered rings of the indenyl ligands (see below).



The search for other routes toward clusters containing indenyl ligands prompted the synthesis of $\text{IrRe}_2(\mu\text{-H})_2(\text{CO})_9(\eta^5\text{-C}_9\text{H}_7)$ from the reaction of $\text{Ir}(\text{CO})(\eta^2\text{-C}_8\text{H}_{14})(\eta^5\text{-C}_9\text{H}_7)$ with $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8$. Deprotonation of $\text{IrRe}_2(\mu\text{-H})_2(\text{CO})_9(\eta^5\text{-C}_9\text{H}_7)$ with KOH/EtOH and addition of $[\text{PPN}][\text{Cl}]$ provided $[\text{PPN}][\text{IrRe}_2(\mu\text{-H})(\text{CO})_9(\eta^5\text{-C}_9\text{H}_7)]$. Addition of PPh_3 to $\text{IrRe}_2(\mu\text{-H})_2(\text{CO})_9(\eta^5\text{-C}_9\text{H}_7)$ led to the carbonyl substitution product $\text{IrRe}_2(\mu\text{-H})_2(\text{CO})_8(\text{PPh}_3)(\eta^5\text{-C}_9\text{H}_7)$, which contains the phosphine ligand on a rhenium atom, as well as to cluster fragmentation.

The reactions of $\text{Ir}(\text{CO})(\eta^2\text{-C}_8\text{H}_{14})(\eta^5\text{-C}_9\text{H}_7)$ with C_2R_2 were explored as an indirect method toward alkyne complexes of $\text{Ir}_3(\mu\text{-CO})_3(\eta^5\text{-C}_9\text{H}_7)_3$. The mononuclear and dinuclear compounds, $\text{Ir}(\text{CO})(\eta^2\text{-C}_2\text{R}_2)(\eta^5\text{-C}_9\text{H}_7)$ and $\text{Ir}_2(\text{CO})_2(\mu\text{-C}_2\text{R}_2)(\eta^5\text{-C}_9\text{H}_7)_2$ were obtained. Also, alkyne coupling and activation of a C-H bond in the arene solvent formed a novel mononuclear compound containing a substituted butadiene ligand (see below).



References

1. (a) Rerek, M. E.; Ji, L.-N.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1983**, 1208.
- (b) Rerek, M. E.; Basolo, F. *J. Am. Chem. Soc.* **1984**, *106*, 5908.
- (c) Kakkar, A. K.; Taylor, N. J.; Marder, T. B.; Shen, J. K.; Hallinan, N.; Basolo, F. *Inorg. Chim. Acta* **1992**, *198-200*, 219.
- (d) Ji, L.-N.; Rerek, M. E.; Basolo, F. *Organometallics* **1984**, *3*, 740.

2. Comstock, M. C.; Wilson, S. R.; Shapley, J. R. *Organometallics* **1994**, *13*, 3805.
3. (a) Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 648; *Angew. Chem.* **1977**, *89*, 671.
(b) Al-Obaidi, Y. N.; Green, M.; White, N. D.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 319.
4. Shapley, J. R.; Adair, P. C.; Lawson, R. J.; Pierpont, C. G. *Inorg. Chem.* **1982**, *21*, 1701.
5. Wadepohl, H.; Gebert, S. *Coord. Chem. Rev.* **1995**, *143*, 535.
6. Braga, D.; Grepioni, F.; Wadepohl, H.; Gebert, S.; Calhorda, M. J.; Veiros, L. F. *Organometallics* **1995**, *14*, 5350.
7. Robben, M. P.; Geiger, W. E.; Rheingold, A. L. *Inorg. Chem.* **1994**, *33*, 5615.