Synthesis and Properties of Mononuclear and Polynuclear Indenyl Iridium Complexes

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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.'

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 Ir(CO)$_2$(η$^5$-C$_9$H$_7$) with Ir(η$^2$-C$_2$H$_4$)$_2$(η$^5$-C$_9$H$_7$) provided Ir$_3$(μ-CO)$_3$-(η$^5$-C$_9$H$_7$)$_3$, and the reaction of Ir(CO)$_2$(η$^5$-C$_9$H$_7$) with Rh(η$^2$-C$_2$H$_4$)$_2$(η$^5$-C$_9$H$_7$) provided the trinuclear clusters Ir$_3$-Rh$_x$(μ-CO)$_3$(η$^5$-C$_9$H$_7$)$_3$ (x = 0 - 2) in good yields, as well as Rh$_3$(μ-CO)$_3$(η$^5$-C$_9$H$_7$)$_3$ which had been studied previously.

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\text{LIr(CO)$_2$ + LRh(η$^2$-C$_2$H$_4$)$_2$ → Hexane, 48 h}$$

$$\text{M = Ir, Rh}$$

These compounds react readily with carbon monoxide to form mononuclear products, whereas the corresponding cyclopentadienyl compounds are much less reactive. 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 M$_3$(CO)$_3$(η$^5$-L)$_3$, where L refers to η$^5$-C$_5$H$_5$ and related ligands. The reaction of the trirhodium cluster Ir$_3$(CO)$_3$(η$^5$-C$_9$H$_7$)$_3$ with HBF$_4$·Et$_2$O gave [Ir$_3$(μ-H)(CO)$_3$(η$^5$-C$_9$H$_7$)$_3$][BF$_4$]. Subsequent deprotection led to generation of C$_{3v}$-Ir$_3$(μ-CO)$_3$(η$^5$-C$_9$H$_7$)$_3$, which rapidly reverted to an equilibrium mixture of major isomer C$_{3v}$-Ir$_3$(μ-CO)$_3$(η$^5$-C$_9$H$_7$)$_3$ and minor isomer C$_6$-Ir$_3$(CO)$_3$(η$^5$-C$_9$H$_7$)$_3$. The solution dynamics and interconversion of both isomers were explored. Variable temperature $^1$H and $^{13}$C NMR experiments indicated that C$_5$-Ir$_3$(CO)$_3$(η$^5$-C$_9$H$_7$)$_3$ undergoes a dynamic process that involves the intermediacy of a third isomer of Ir$_3$(CO)$_3$(η$^5$-C$_9$H$_7$)$_3$. This study provides a unique set of relative energies in solution for three of the four observed forms for a M$_3$(CO)$_3$(η$^5$-L)$_3$ system.

The reactions of C$_{3v}$-Ir$_3$(μ-CO)$_3$(η$^5$-C$_9$H$_7$)$_3$ with metal fragment electrophiles containing Cu, Ag, Au, and Hg provided cationic tetranuclear clusters, which show a rearrangement of the Ir$_3$(η$^5$-C$_9$H$_7$)$_3$ moiety to a C$_5$ geometry. The reaction with TIPF$_6$ gave [Ir$_3$TI(μ-CO)$_3$(η$^5$-C$_9$H$_7$)$_3$][PF$_6$], which maintains the C$_{3v}$ geometry of C$_{3v}$-Ir$_3$(μ-CO)$_3$(η$^5$-C$_9$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 IrRe$_2$(μ-H)$_2$(CO)$_9$($\eta^2$-C$_8$H$_{14}$($\eta^5$-C$_9$H$_7$)) from the reaction of Ir(CO)($\eta^2$-C$_8$H$_{14}$($\eta^5$-C$_9$H$_7$)) with Re$_2$(μ-H)$_2$(CO)$_8$. Deprotonation of IrRe$_2$(μ-H)$_2$(CO)$_9$($\eta^5$-C$_9$H$_7$) with KOH/EtOH and addition of [PPN][Cl] provided [PPN][IrRe$_2$(μ-H)(CO)$_9$($\eta^5$-C$_9$H$_7$)]. Addition of PPh$_3$ to IrRe$_2$(μ-H)$_2$(CO)$_9$($\eta^5$-C$_9$H$_7$) led to the carbonyl substitution product IrRe$_2$(μ-H)$_2$(CO)$_8$-(PPh$_3$($\eta^5$-C$_9$H$_7$), which contains the phospine ligand on a rhenium atom, as well as to cluster fragmentation.

The reactions of Ir(CO)($\eta^2$-C$_8$H$_{14}$($\eta^5$-C$_9$H$_7$)) with C$_2$R$_2$ were explored as an indirect method toward alkyne complexes of Ir$_3$(μ-CO)$_3$($\eta^5$-C$_9$H$_7$)$_3$. The mononuclear and dinuclear compounds, Ir(CO)($\eta^2$-C$_2$R$_2$)$_2$($\eta^5$-C$_9$H$_7$) and Ir$_2$(CO)$_2$(μ-C$_2$R$_2$)$_2$($\eta^5$-C$_9$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

   (d) Ji, L.-N.; Rerck, M. E.; Basolo, F. Organometallics 1984, 3, 740.


