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Preliminary communication

GROUP IVB—RHODIUM COMPLEXES: NEW ORGANORHODIUM ANIONS IN SYNTHESIS

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Summary

The novel anions $[Rh(X)(CO)(\eta^5\text{-}C_5H_5)]^-$ (X = H, $GeMe_3$) have been produced, and employed as an entry into organo-Group IVB—rhodium chemistry.

The similarities in the chemistry of $Fe(CO)_5$ and of the complexes $M(CO)_2(\eta^5\text{-}C_5H_5)$ (M = Co, Rh, Ir) have often been referred to. However, although $Fe(CO)_5$ is known [1] to yield the anionic complexes $[Fe(CO)_4]^{2-}$ and $[Fe(H)(CO)_4]^-$ which have been instrumental in the development of carbonyliron chemistry, no comparable species have been derived from $M(CO)_2(\eta^5\text{-}C_5H_5)$. In this communication we describe two such organorhodium anions, and illustrate their utility in the synthesis of organo-Group IVB—rhodium complexes.

Treatment of either $Rh(CO)_2(\eta^5\text{-}C_5H_5)$ or $Rh(I)_2(CO)(\eta^5\text{-}C_5H_5)$ [2] briefly in tetrahydrofuran with a sodium amalgam gives an air-sensitive yellow-black solution with properties characteristic of its containing $[Rh(H)(CO)(\eta^5\text{-}C_5H_5)]^-$. Attempts to isolate this anion by precipitation with large counter ions have so far been unsuccessful. The IR spectrum of the solution, however, shows a single carbonyl absorption at 1892 cm^{-1}, typical of a uninegative anion rather than of $[Rh(CO)(\eta^5\text{-}C_5H_5)]^{2-}$. The existence of the related $[Fe(H)(CO)_4]^-$ in aqueous solution is well established [3], and it seems likely that in the presence of traces of water in the solvent $[Rh(H)(CO)(\eta^5\text{-}C_5H_5)]^-$ is formed here.

Reaction of the anion solution with trimethylbromogermane or trimethylchlorostannane yields (20-30%) very pale yellow low-melting complexes $Rh(MMe_3)_2(CO)(\eta^5\text{-}C_5H_5)$ (M = Ge, Sn [4]) (for M = Ge, ν(CO) (hexane) 1995 cm^{-1}; τ 4.70(5H), 9.59(18H)); products which are not inconsistent with $[Rh(H)(CO)(\eta^5\text{-}C_5H_5)]^-$ being the effective nucleophile [5]. Significantly, a very air-sensitive pale yellow liquid isolated as a minor product of the reaction with Me_3SnCl was identified from its IR (ν(CO) 1999 cm^{-1})

and mass $((M - H - n\mathrm{CO})^+, (n = 0, 1))$ spectra as $\mathrm{Rh(H)(SnMe_3)(CO)(\eta^5\text{-}C_5H_5)}$ Only IR-observable quantities of $\mathrm{Rh(PbMe_3)_2(CO)(\eta^5\text{-}C_5H_5)}$ were obtained from the anion and $\mathrm{Me_3PbCl}$, but the known [4] tin—rhodium heterocycle $\mathrm{[Rh(\mu\text{-}SnMe_2)(CO)(\eta^5\text{-}C_5H_5)]_2}$ was characterised as a product of the reaction with $\mathrm{Me_2SnCl_2}$.

Reaction of $\mathrm{Rh(MMe_3)_2(CO)(\eta^5\text{-}C_5H_5)}$ (M = Ge, Sn) with iodine in hexane at room temperature proceeds rapidly with cleavage of one Rh—$\mathrm{MMe_3}$ bond, forming (50-55%) $\mathrm{Rh(I)(MMe_3)(CO)(\eta^5\text{-}C_5H_5)}$. The dark-red crystalline germanium complex (m.p. 79-80°; ν(CO) 2031 $\mathrm{cm^{-1}}$; τ 4.35 (5H), 9.09(9H)) may be reduced with sodium amalgam in tetrahydrofuran to produce an air-sensitive solution with the reactivity anticipated of the $\mathrm{[Rh(GeMe_3)(CO)(\eta^5\text{-}C_5H_5)]^-}$ anion (again, efforts to isolate this species as a salt have been unsuccessful). Thus, on reaction with $\mathrm{Me_3SnCl}$ pale yellow liquid $\mathrm{Rh(GeMe_3)(SnMe_3)(CO)(\eta^5\text{-}C_5H_5)}$ (ν(CO) 1989 $\mathrm{cm^{-1}}$; τ 4.71(5H), 9.57(9H), 9.67(9H)) is formed (40%). Minor products $\mathrm{Rh(MMe_3)_2(CO)(\eta^5\text{-}C_5H_5)}$ (M = Ge, Sn) were also obtained, indicating that the anion $\mathrm{[Rh(GeMe_3)(CO)(\eta^5\text{-}C_5H_5)]^-}$ may disproportionate to some small extent in solution to give $\mathrm{Rh(GeMe_3)_2(CO)(\eta^5\text{-}C_5H_5)}$ and $\mathrm{[Rh(CO)(\eta^5\text{-}C_5H_5)]^{2-}}$ (presumably converted to $\mathrm{[Rh(H)(CO)(\eta^5\text{-}C_5H_5)]^-}$). It is interesting to note that iodine preferentially cleaves the Rh—Sn bond of $\mathrm{Rh(GeMe_3)(SnMe_3)(CO)(\eta^5\text{-}C_5H_5)}$, forming $\mathrm{Rh(I)(GeMe_3)(CO)(\eta^5\text{-}C_5H_5)}$ exclusively.

Finally, we wish to report that a surprising reaction occurs between $\mathrm{Rh(I)(GeMe_3)(CO)(\eta^5\text{-}C_5H_5)}$ and $\mathrm{(\eta^1\text{-}C_5H_5)SnPh_3}$, giving in high yield red crystalline $\mathrm{Rh(I)(SnPh_3)(CO)(\eta^5\text{-}C_5H_5)}$ (m.p. 155-156°; ν(CO) 2031 $\mathrm{cm^{-1}}$; τ 2.3-2.7(15H), 4.20(5H)). The anticipated formation of an $\mathrm{\eta^1\text{-}C_5H_5}$ derivative of rhodium is evidently unfavourable relative to an exchange of Group IVB ligands similar to that observed [6] for organogermanium—ruthenium complexes upon reaction with organotin hydrides.

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