Journal of Organometallic Chemistry, 214 (1981) C43—C44
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

SYNTHESIS AND CHARACTERIZATION OF [PPN][$HRu(CO)_4$] AND A CONVENIENT ROUTE TO [PPN][$HOs(CO)_4$]

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(Received December 16th, 1980)

Summary

Simple high yield syntheses of the previously unreported anion $HRu(CO)_4^-$ and of the osmium analog $HOs(CO)_4^-$ as the PPN^+ salts are presented with infrared and ^1H NMR data

We report convenient syntheses of the $HRu(CO)_4^-$ anion and of the known $HOs(CO)_4^-$ anion as PPN^+ salts (PPN^+ = bis(triphenylphosphine)iminium). L'Epplattinier has reported the synthesis of $HOs(CO)_4^-$ by sodium sand reduction of $H_2Os(CO)_4$ [1], and the properties of the iron analog have been well studied [2]. In conjunction with our studies of the acid-base properties of the metal carbonyl hydrides [3], and with the proposed role of mononuclear ruthenium carbonyl hydrides (including $HRu(CO)_4^-$) in the homogeneous catalysis of the water-gas shift reaction [4—6] and of ethylene glycol synthesis [7], we sought to prepare and characterize the previously unknown $HRu(CO)_4^-$ ion.

[PPN][$HRu(CO)_4$] can be obtained in 60% yield by dissolution of $Na_2Ru(CO)_4$ in a minimum volume of methanol, addition of PPN^+Cl^- and filtration at −78°C. The $Na_2Ru(CO)_4$ is obtained by reducing $Ru_3(CO)_{12}$ (100 mg, 0.16 mmol) with sodium in liquid ammonia [8]. Residual ammonia is removed in vacuo at room temperature for four hours. Methanol (10 ml) is condensed onto the $Na_2Ru(CO)_4$ at −196°C and the flask is warmed to −78°C under nitrogen. PPN^+Cl^- (300 mg, 0.52 mmol) in methanol (5 ml) is added slowly to the solution. The flask is then removed from the −78°C bath and allowed to warm until precipitation of off-white product begins. Care must be taken to keep the solution cold to minimize cluster formation. We attribute the cluster formation to the production of a small, equilibrium amount of $H_2Ru(CO)_4$ which then further reacts forming the $HRu_3(CO)_{11}^-$ ion as a final product [5]. The solution is returned to the −78°C bath and the solid col-

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lected by filtration under nitrogen through a dry ice-chilled frit. The product is dried in vacuo and recrystallized from THF/hexane. (Anal. Found: C, 63.38; H, 4.12; N, 2.37; P, 8.09. Calcd. for [PPN][$HRu(CO)_4$]: C, 63.83; H, 4.15; N, 1.86; P, 8.23%). [PPN][$HRu(CO)_4$] in THF shows infrared absorptions at 2003w, 1925m and 1885s cm^{-1}. A single high field resonance is observed in the ^1H NMR at τ 17.77 in acetone-d_6. The product is moderately air stable as a solid and in THF solutions. Addition of water to a THF solution, or dissolution of the anion in neutral methanol results in the aforementioned formation of $HRu_3(CO)_{11}^-$ at room temperature [9].

Synthesis of $H_2Os(CO)_4$ without recourse to high pressure equipment [10] is accomplished by protonation of $Na_2Os(CO)_4$ [10]. The latter is obtained by sodium reduction of $Os_3(CO)_{12}$ in liquid ammonia [11]. We have found that [PPN][$HOs(CO)_4$] can be isolated in high yield in the same manner as described for [PPN][$HRu(CO)_4$]. (Anal. Found: C, 57.83; H, 3.85; N, 2.02. Calcd. for [PPN][$HOs(CO)_4$]: C, 57.07; H, 3.71; N, 1.66%. A THF solution exhibits infrared absorptions at 2110m, 1949m and 1884s cm^{-1}. The ^1H NMR shows a single high field resonance at τ 20.15 in acetone-d_6 [12].

The synthesis of $HRu(CO)_4^-$ completes the triad of compounds of the type $HM(CO)_4^-$ (M = Fe, Ru, Os). The similarity in the band positions and intensities in the infrared spectra of the three analogous compounds suggests structural similarity. The wide variety of reactivity of derivatives of the iron triad carbonyl hydrides [13] and their catalytic importance makes the study of the chemistry of the heavier metal analogs intriguing. The unique catalytic properties of ruthenium carbonyl may be related to the thermal instability of $H_2Ru(CO)_4$ (like that of $H_2Fe(CO)_4$) coupled to its weak acidity [14] (like that of the osmium analog). The availability of $HRu(CO)_4^-$ will make studies of these properties possible.

Acknowledgements

This research received partial support from the National Science Foundation (grant no. CH 77-27415 to R.G. Pearson) and the Department of Energy, Office of Basic Sciences (contract no. E Y-76-S03-0034, PA 262 with P.C. Ford).

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