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Synthesis, oxidation and acid reactions of dinuclear cyclopentadienylrhodium carbonyl phosphine compounds

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Abstract

The dinuclear rhodium compounds $(\eta^5:\eta^5\text{-}C_{10}H_8)[Rh(CO)_2]_2$, $CH_2[\eta^5\text{-}C_5H_4Rh(CO)_2]_2$ and $CH_2[\eta^5\text{-}C_5H_4Rh(CO)]_2\text{-}\mu\text{-}CO$ react with triphenylphosphine to give rhodium carbonyl phosphine derivatives. Reactions of $(\eta^5:\eta^5\text{-}C_{10}H_8)[Rh(CO)_2]_2$ with bis(diphenylphosphino)methane and either $CH_2[\eta^5\text{-}C_5H_4Rh(CO)_2]_2$ or $CH_2[\eta^5\text{-}C_5H_4Rh(CO)]_2\text{-}\mu\text{-}CO$ with tetramethyldiphosphine give products in which the diphosphine ligand links the two metal atoms. $CH_2\{\eta^5\text{-}C_5H_4Rh(CO)[(C_6H_5)_3P]\}_2$ reacts with acids to form a stable, doubly protonated dication and does not give an identifiable product upon oxidation with ferrocinium hexafluorophosphate. In contrast, $(\eta^5:\eta^5\text{-}C_{10}H_8)[Rh(CO)]_2\text{-}\mu\text{-}[(C_6H_5)_2P]_2CH_2$ and $CH_2[\eta^5\text{-}C_5H_4Rh(CO)]_2\text{-}\mu\text{-}(CH_3)_4P_2$ react both with acids and ferrocinium hexafluoroborate to give stable, diamagnetic dications which must possess Rh–Rh bonds. Reactions with acids are accompanied by dihydrogen evolution. Similarly, oxidations of $(\eta^5:\eta^5\text{-}C_{10}H_8)[Rh(CO)_2]_2$ and $CH_2[\eta^5\text{-}C_5H_4Rh(CO)_2]_2$ with ferrocinium hexafluoroborate yield diamagnetic, dicationic products. Analogous results have been previously reported for interactions of $(\eta^5:\eta^5\text{-}C_{10}H_8)\{Rh(CO)[(C_6H_5)_3P]\}_2$ with acids and with ferrocinium hexafluoroborate.

Introduction

Dinuclear transition metal compounds such as **1**, **2** and **3** have been shown to react with strong acids such as HBF_3OH to liberate dihydrogen [1]. In the case of **1**, the resulting organometallic dication is stable and can be reduced either chemically

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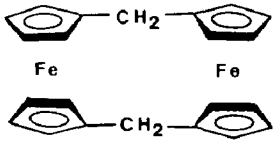
or electrochemically to the starting, neutral compound. The ability of **1** to cycle through a redox process in which dihydrogen is liberated suggests that it, or other related compounds, might be of importance in devices designed to photoelectrochemically generate dihydrogen from water [2]. Such a device in which polymer bound derivatives of **1** are coated on a p-type semiconductor has been reported by Muller–Westerhoff and Nazzal [3]. While these workers have demonstrated the feasibility of using dinuclear compounds, the low basicity of ferrocene might be a disadvantage and it clearly would be preferable to use systems with higher basicity. In general, compounds for use in these devices must be air stable, have a high metal basicity, and yield a stable dication which can be reduced back to the starting, neutral compound.



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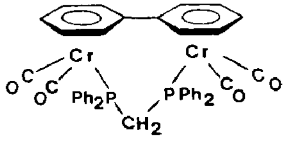

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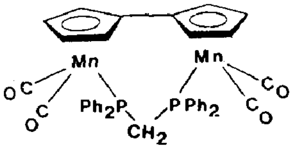

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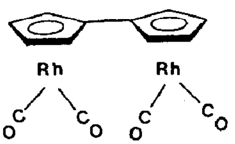
Reports in the literature [4] and our own examination of the protonation of cyclopentadienylrhodium compounds [5] suggested that dinuclear, bridged organorhodium compounds might be ideal candidates for studying dihydrogen liberation.

Results and discussion

We have recently reported the synthesis of the dinuclear rhodium compounds $(\eta^5:\eta^5\text{-}C_{10}H_8)[Rh(CO)_2]_2$ (**4**) and $CH_2[\eta^5\text{-}C_5H_4Rh(CO)_2]_2$ (**5**) by reaction of $[ClRh(CO)_2]_2$ with either fulvalenedithallium [6] or bis(cyclopentadienylthallium)-methane [7], respectively. Dinuclear compound **5** readily loses carbon monoxide on



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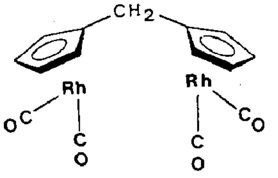

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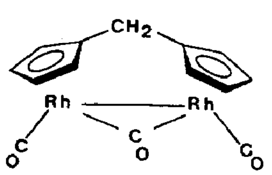

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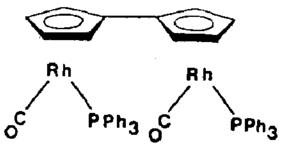

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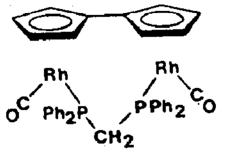

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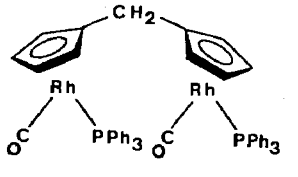
reflux in benzene to form $CH_2[\eta^5\text{-}C_5H_4Rh(CO)]_2\text{-}\mu\text{-}CO$ (**6**). We have subsequently found that reactions of either **5** or **6** with triphenylphosphine or tetramethyldiphosphine in refluxing hexane produce the appropriate phosphine complexes **8**, **10** and **11** in good yield. Likewise, reactions of **4** with either bis(diphenylphosphino)methane or triphenylphosphine under similar conditions yield the respective phosphine analogues **7** and **8**. Complex **7** has previously been reported by Connelly and coworkers [8].



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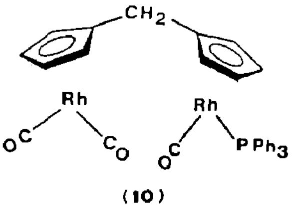

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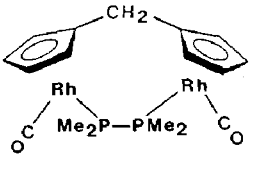
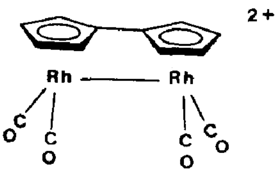
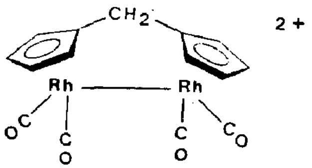


(**11**)

Chemical oxidation of **4** and **5** using ferrocinium hexafluorophosphate in dichloromethane gives the diamagnetic dicationic compounds **12** and **13**, isolated as bis(hexafluorophosphate) salts. It should be noted that attempts to study the electrochemistry of cyclopentadienylrhodium dicarbonyl indicate that this compound undergoes irreversible oxidation to unidentified products [9]. Apparently the formation of a Rh–Rh bond by the oxidized species in the dinuclear systems occurs more rapidly than the radical decomposition pathway. The dicationic compounds **12** and **13** were stable in air, but the solids underwent decomposition over several days to give new cationic species of unknown structure.

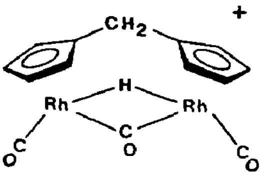


(**12**)



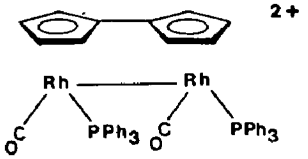
(**13**)

Addition of trifluoromethanesulfonic acid, CF_3SO_3H, to solutions of **4** gave no apparent reaction, but **5** did react under these conditions to give a mixture of **13** and **14**. **14** can also be formed by the direct protonation of **6** [7]. Herrmann and coworkers [10] have reported that pentamethylcyclopentadienylrhodium dicarbonyl reacts with acids to form an analogous, protonated dinuclear species, $\{[(Me_5C_5)Rh(CO)]_2(\mu\text{-}CO)(\mu\text{-}H)\}^+$.



As previously reported by Connelly [8a], **7** reacts with either ferrocinium hexafluorophosphate or HBF_4 to give a diamagnetic dication, **15**. Dihydrogen is evolved in the acid reaction. Similarly, **8** reacts with either ferrocinium hexafluorophosphate of $HBF_4 \cdot OEt_2$ to form the diamagnetic dication, **16**, which can be reduced back to its neutral form by reaction with NaK. Reaction with $HBF_4 \cdot OEt_2$ is also accompanied by rapid dihydrogen evolution.

Reaction of **9** with CF_3SO_3H in $CDCl_3$ was found to give the diprotonated species **17** which was stable in acid solutions for extended periods. When the somewhat weaker acid, CF_3CO_2H was added to solutions of **9** in $CDCl_3$, a spectrum intermediate between that of **9** and **17** was observed, suggesting that rapid hydrogen exchange between the solute and the acid was occurring. This is in contrast to the analogous mononuclear compound, cyclopentadienylrhodium carbonyl triphenylphosphine, which is completely protonated by CF_3CO_2H under these conditions [5]. Werner and coworkers [11] have shown that the closely related dinuclear compound, $CH_2[(C_5H_4)Rh(CO)PMe_3]_2$, is also protonated by CF_3SO_3H to give a species which could be isolated as its hexafluorophosphate salt.



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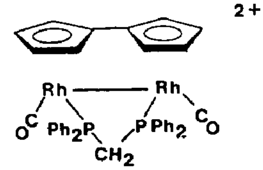

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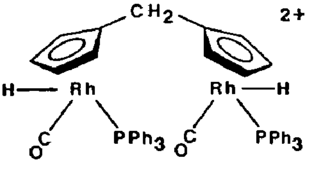

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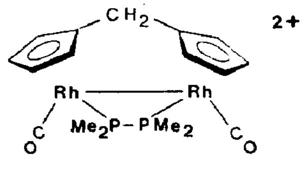
Oxidation of **9** with ferricinium hexafluorophosphate gave a black solid which was shown by IR to have no carbonyl stretching bands. The ^1H NMR spectrum of this material is complex and it has not been possible to establish its identity.

Reaction of **11** with either $HBF_4 \cdot OEt_2$ or ferrocinium hexafluorophosphate resulted in the formation of the stable dicationic species, **18**, which was characterized by its IR spectrum. Because of the limited quantities of this material which were available, a detailed study of its chemistry was not carried out.



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In summary, we have shown that several bridged dinuclear organorhodium compounds undergo chemical oxidation to yield stable diamagnetic dications which presumably contain Rh–Rh bonds. Compounds **4**, **7**, **8** and to some extent **5** react with acid to liberate dihydrogen and form dications that are identical to those produced by chemical oxidation. The failure of **9** to yield a recognizable oxidation product and its reaction with acid to yield a stable protonated species suggests that in this case steric constraints preclude the required close approach of the two metal atoms. Preliminary studies on the iridium analogues of **5** and **9** indicate that these compounds follow a very similar set of reactions except that no iridium analog of **14** was observed [12].

Experimental

Preparations of compounds **4**, **5**, and **6** from their appropriate thallium precursors have been published previously [6,7]. Bis(diphenylphosphino)methane [13] and tetramethyldiphosphine [14] were prepared by literature procedures. Triphenylphosphine, tetrafluoroboric acid diethyletherate, trifluoromethanesulfonic acid, and trifluoroacetic acid were purchased from Aldrich and used as received. Ferrocinium hexafluorophosphate was a generous gift of Prof. William Geiger and Dr. Norman Van Order. All solvents were dried and distilled under nitrogen. All reactions were conducted under nitrogen. Preparative chromatography was conducted under nitrogen using CAMAG neutral grade alumina (Aldrich).

Infrared spectra were recorded on a Perkin–Elmer 1750 FTIR Spectrometer. NMR spectra were recorded on a Varian Associates FT 80A NMR Spectrometer operating at 79.543 MHz (^1H) or 32.197 MHz (^{31}P). NMR spectra are referenced to either internal tetramethylsilane, TMS, or to external 85% H_3PO_4. All phosphorus spectra are broad band proton decoupled. Coupling constants for second order ^{31}P NMR spectra were calculated using the SIMEQ spectral simulation program on the Varian FT 80A Spectrometer. Elemental analyses were conducted by the Microanalysis Laboratory of the University of Massachusetts, Amherst, MA 01003.

Synthesis of $C_{10}H_8[Rh(CO)]$-μ-$(Ph_2P)_2CH_2$ *(8)*

Compound **4** (0.50 g, 1.1 mmol) and $(Ph_2P)_2CH_2$ (0.42 g, 1.1 mmol) together with 100 ml of hexane were added to a 200 ml round bottom flask equipped with a spin bar and West condenser. The mixture was refluxed for 6 h at which time a red oil separated from the hexane solution. After cooling the oil solidified to give an air stable orange powder which was collected by filtration. The powder was taken up in a minimum quantity of 1/1 ligroin/dichloromethane and chromatographed on a 30 cm × 2 cm alumina column. Minor bands of unreacted starting materials were occasionally observed and eluted before the main orange band containing the product. The product band was collected under nitrogen and solvent was removed to give an orange powder, m.p. 210 ° C with decomposition. Analytical samples were further purified by recrystallization from dichloromethane/ligroin. Yield 0.39 g (45%). IR (CH_2Cl_2): 1944 cm^{-1} (d). ^1H NMR ($CDCl_3$): 7.98–7.25 (20 H), 5.37 (4H), 4.75 (4H), 3.25 (t, 2H, J(P–H) 9.2 Hz). ^{31}P NMR ($CDCl_3$): 40.54 (d of t, J(Rh(A)–P(a)) 207 Hz, J(P(a)–P(b)) 49 Hz, J(Rh(A)–P(b)) 2 Hz). Analysis: Found: C, 57.35; H, 4.07; P. 8.17. $C_{37}H_{30}O_2P_2Rh_2$ calcd.: C, 57.36; H, 3.88; P, 8.01%.

Compounds **7**, **9**, **10**, and **11** were prepared by similar procedures.

7. Red orange powder. IR (CH_2Cl_2): 1940 (s) cm^{-1}. ^1H NMR ($CDCl_3$): 7.55–7.34 (30 H), 5.03 (8H). ^{31}P NMR ($CDCl_3$): 31.34 (d, J(Rh–P) 199.62 Hz).

9. Red orange powder, m.p. 122–123° C, yield 95%. IR (CH_2Cl_2): 1940 (s) cm^{-1}. ^1H NMR ($CDCl_3$): 7.56–7.27 (30H), 5.18 (4H), 4.83 (4H), 3.06 (2H). ^{31}P NMR ($CDCl_3$): 52.81 (d, J(Rh–P) 199.55 Hz). Analysis: Found: C, 63.17; H, 4.24; P, 6.40. $C_{49}H_{40}O_2P_2Rh_2$ calcd.: C, 63.36; H, 4.31; P, 6.68%.

10. Red oil. IR (CH_2Cl_2): 2038 (s), 1968 (s), 1942 (s) cm^{-1}. ^1H NMR ($CDCl_3$): 7.69–7.28 (15H), 5.43 (2H), 5.24 (4H), 4.90 (2H), 3.16 (2H). ^{31}P NMR ($CDCl_3$): 52.65 (d, J(Rh–P) 198.49 Hz).

12. Red oil. IR (CH_2Cl_2): 1936 (s) cm^{-1}. ^1H NMR ($CDCl_3$): 5.40 (4H), 4.99 (4H), 3.50 (2H), 3.36 (t, 12H, J(P–H) 2 Hz). ^{31}P NMR ($CDCl_3$): 20.10 (d of t, J(Rh(A)–P(a)) 190 Hz, J(P(a)–P(a)) 111 Hz).

Oxidation of rhodium compounds by ferrocinium hexafluorophosphate

The rhodium compounds, 100–200 mg, were dissolved in dichloromethane and

added slowly to solutions of two equivalents of ferrocinium hexafluorophosphate in dichloromethane. The oxidations were rapid and completion was indicated by the disappearance of the blue ferrocinium color. After about 2 h the solutions were concentrated and hexane was added to precipitate the oxidized rhodium complexes which were collected by filtration. The compounds are air stable, but sensitive to water. An IR band at about 847 cm^{-1} was associated with the hexafluorophosphate.
12. IR: (CH_3NO_2) 2128 (s), 2099 (s) cm^{-1}. ^1H NMR (acetone-d_6): 7.56 (4H), 5.99 (4H). Decomposition product of **12** has IR bands at 2150 (s) and 2117 (s) cm^{-1}.
13. IR: (CH_2NO_2) 2142 (s), 2112 (s) cm^{-1}. ^1H NMR (acetone-d_6): 6.56 (4H), 5.98 (4H), 4.12 (2).
12. IR: (CH_3NO_2) 2079 (s), 2048 (m) cm^{-1}. ^1H NMR (acetone-d_6): 7.90–7.44 (20H), 7.29 (2H), 6.43 (2H), 5.77 (4H), 5.38 (t, 2H, J(P–H) 13.03 Hz). ^{31}P NMR (acetone-d_6): 28.20 (d of t, J(Rh(A)–P(a)) 143 Hz, J(P(a)–P(b)) 45 Hz). Analysis: Found: C, 41.97; H, 2.71; P, 11.35. $C_{37}H_{30}O_2P_4F_{12}Rh_2$ calcd.: C, 41.73; H, 2.83; P, 11.65%.
18. IR (CH_3NO_2): 2072 (s), 2042 (m) cm^{-1}.
Compound **15** has been described previously [8].

Reactions of rhodium compounds with acids

Standard 5 mm NMR tubes were charged with about 20 mg of rhodium compound, evacuated and backflushed with nitrogen. $CDCl_3$ was added to the tubes and their ^1H NMR spectrum recorded. About 10 μl of appropriate acid was added to the tubes and the spectra recorded immediately. Both ^1H and ^{31}P NMR spectra were recorded within five min of mixing.

Protonation of **5** with CF_3CO_2H to give **14**: ^1H NMR ($CDCl_3$ + TFA): 6.24 (4H), 6.00 (4H), 3.37 (2H), −10.47 (1H, t, J(Rh–H) 18.3 Hz).

Protonation of **9** with CF_3SO_3H to give **17**: ^1H NMR ($CDCl_3$ + CF_3SO_3H): 7.59–7.25 (30H), 6.10 (2H), 5.85 (2H), 5.42 (2H), 5.25 (2H), 3.32 (2H), −9.61 (2H, d of d, J(Rh–H) 21.80 Hz, J(P–H) 17.20 Hz). ^{31}P NMR ($CDCl_3$): 43.77 (d, J(Rh–P) 121.07).

Protonation of **9** with CF_3CO_2H: ^1H NMR ($CDCl_3$ + CF_3CO_2H): 7.65–7.25 (30H), 5.82 (4H), 5.44 (4H), 3.36 (2H). ^{31}P NMR ($CDCl_3$ + TFA): 43.61 (d, J(Rh–P) 120.20 Hz). Note Rh–H resonance not observed in ^1H NMR suggests rapid exchange with CF_2CO_2H.

Reactions of 7, 8, and 11 with HBF_4 etherate

About 50 mg of rhodium compound was placed in a 20 ml Schlenk flask and the flask evacuated and backflushed with nitrogen. Five ml of dichloromethane was added followed by several drops of acid. Compounds **7**, **8**, and **11** reacted immediately to give solids which were shown by NMR and IR spectra to be identical (except for counterion) to those produced by ferrocinium oxidation.

Acknowledgement

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References

1 (a) T.E. Bitterwolf and A.C. Ling, J. Organomet. Chem., 57 (1973) C15; (b) T.E. Bitterwolf, ibid., 252 (1983) 305; (c) T.E. Bitterwolf and K.S. Raghuveer, New J. Chem., submitted.

2 T.E. Bitterwolf, Polymer Bound Bimetallic Complexes as Surface Reactants on Semiconductor Electrodes in C. Carraher, J. Sheats and C. Pittman (Eds.), Organometallic and Inorganic Polymers, Plenum Press, New York, 1985.

3 (a) U.T. Mueller-Westerhoff and A. Nazzal, J. Am. Chem. Soc., 106 (1984) 5381; (b) U.T. Mueller-Westerhoff and A. Nazzal, U.S. Patent 4,379,740, 12 April, 1983.

4 (a) H. Werner, Pure Appl. Chem., 54 (1982) 177; (b) H. Werner, Angew. Chem., Int. Ed., 22 (1983) 927.

5 T.E. Bitterwolf, Inorg. Chim. Acta, 122 (1986) 175.

6 M.D. Rausch and W.C. Spink, J. Organomet. Chem., 308 (1986) C1.

7 T.E. Bitterwolf, J. Organomet. Chem., 312 (1986) 197.

8 (a) N.G. Connelly, A.R. Lucy, J.D. Payne, A.M.R. Galas, and W.E. Geiger, J. Chem. Soc., Dalton Trans., (1983) 1879; (b) M.J. Freeman, A.G. Orpen, N.G. Connelly, I. Manners, and S.J. Raven, J. Chem. Soc., Dalton Trans., (1985) 2283.

9 W.G. Geiger and T. Gennett, personal communication, 1987.

10 (a) W.A. Herrmann, J. Plank, C. Bauer, M.L. Ziegler, E. Guggolz, and R. Alt, Z. Anorg. Allg. Chem., 487 (1982) 85; (b) J. Plank, D. Riedel, and W.A. Herrmann, Angew. Chem., Int. Ed., 19 (1980) 937.

11 H. Werner, J.J. Scholz, and R. Zolk, Chem. Ber., 118 (1985) 4531.

12 T.E. Bitterwolf, unpublished results, 1988.

13 S.A. Butter and J. Chatt, Inorg. Syn., 15 (1974) 185.

14 W. Hewertson and H.R. Watson, J. Chem. Soc., (1962) 1490.