11. It is possible to check (by infrared techniques) that the reaction has occurred completely:
$[Rh_2(\mu\text{-}Cl)_2(CO)_4]\nu CO(cm^{-1})$: 2105 m, 2089 vs, 2034 vs
$[Rh_2(\mu\text{-}Cl)(\mu\text{-}t\text{-}C_4H_9S)(CO)_4]$: 2088 m, 2072 vs, 2014 vs
$[Rh_2(\mu\text{-}t\text{-}C_4H_9S)_2(CO)_4]$: 2067 m, 2047 vs, 1998 vs

25. DINUCLEAR METHOXY, CYCLOOCTADIENE, AND BARRELENE** COMPLEXES OF RHODIUM(I) AND IRIDIUM(I)

Submitted by R. USON,* L. A. ORO,* and J. A. CABEZA*
Checked by H. E. BRYNDZA† and M. P. STEPRO†

Bis(η^4-cyclooctadiene)-di-μ-methoxy dirhodium(I), $[Rh(OMe)(1,5\text{-}cod)]_2$, has been prepared by the reaction of $[RhCl(1,5\text{-}cod)]_2$ with sodium carbonate in refluxing methanol,[1] or $[Rh(1,5\text{-}cod)(indole)]ClO_4$ with potassium hydroxide in methanol.[2] The latter method has also been used for the synthesis of analogous derivatives containing tetrafluorobenzobarrelene,‡ $[Rh(OMe)(tfb)]_2$, and trimethyltetrafluorobenzobarrelene $[Rh(OMe)(Me_3tfb)]_2$.[2] The dioxygen-bridged complex $[Rh_2(O_2)(1,5\text{-}cod)_2]$ reacts with methanol or water to give $[Rh(OMe)(1,5\text{-}cod)]_2$ or the hydroxo-bridged complex $[Rh(OH)(1,5\text{-}cod)]_2$.[3]

Bis(η^4-cyclooctadiene)-di-μ-methoxy diiridium(I), $[Ir(OMe)(1,5\text{-}cod)]_2$, has been synthetized from three different starting materials, $[IrCl(1,5\text{-}cod)]_2$,[4] $[IrHCl_2(1,5\text{-}cod)]_2$,[5] or $[Ir(1,5\text{-}cod)_2][BF_4]$[6] by allowing them to react with sodium carbonate in methanol.

The methoxide ion is a strong base, capable of taking a proton from any acid stronger than methanol. The methoxy-bridged complexes have been used both for synthetic purposes[7] and as homogeneous catalyst precursors.[8]

If potassium hydroxide is substituted for sodium carbonate in the preparation of methoxy-bridged derivatives from chloro-bridged complexes, the reactions take place readily under mild conditions, and lead to excellent yields. The use of water as a precipitating agent and as a washing fluid is of great importance, and its use in previously-described processes increases the yields. The syntheses of several methoxy-bridged complexes of rhodium(I) or iridium(I), along with

---

*Department of Inorganic Chemistry, University of Saragossa, Saragossa, Spain.

**Barrelene = bicyclo[2.2.2.]octa-2,5,7-triene.

†Central Research and Development Department, E. I. du Pont de Nemours and Co., Wilmington, DE 19898.

†Tetrafluorobenzobarrelene = 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene.

the preparation of bis(η^4-1,5-cyclooctadiene)-di-μ-hydroxo-dirhodium(I) are described herein.

A. BIS(η^4-1,5-CYCLOOCTADIENE)-DI-μ-METHOXY-DIRHODIUM(I)

$$[RhCl(1,5\text{-cod})]_2 + 2\ KOH + 2\ MeOH \longrightarrow [Rh(OMe)(1,5\text{-cod})]_2 + 2\ KCl + 2\ H_2O$$

Procedure

A 50-mL round-bottomed flask containing a magnetic stirring bar is charged with a solution of $[RhCl(1,5\text{-cod})]_2$[9] (175 mg, 0.355 mmole) in dichloromethane (15 mL). The addition of a solution of potassium hydroxide (40 mg, 0.713 mmole) in methanol (5 mL) gives rise to the immediate precipitation of a yellow solid. After being stirred for 30 minutes at room temperature, the solvent is completely removed in a rotary evaporator. Then, 10 mL of methanol and subsequently 15 mL of water are added to the residue, after which the solid is collected by filtration using a fine sintered-glass filter, washed with water (ten 5-mL portions) and vacuum-dried over phosphorus(V) oxide. Yield: 157 mg (92%). The crude product can be used without further purification. An analytically pure sample can be obtained by recrystallization from a mixture of dichloromethane and hexane. *Anal.* Calcd. for $C_{18}H_{30}O_2Rh_2$: C, 44.65; H, 6.24. Found: C, 44.90; H, 6.20.

Properties

The yellow, air-stable compound is soluble in dichloromethane and chloroform, slightly soluble in benzene and acetone, less soluble in diethyl ether and hexane, and insoluble in water. On being heated, it decomposes between 120–175°. Its ^1H nmr spectrum ($CDCl_3$, TMS) shows three, broad multiplets at δ3.55 (8H, vinylic protons), 2.47 (8H, allylic protons) and 1.63 (8H, allylic protons), along with a sharp singlet at δ2.67 (6H, methoxide). IR (Nujol, cm^{-1}): 3328(m, br), 1330(m), 1304(m), 1231(w), 1214(w), 1154(w), 1078(vs), 998(m), 953(s), 892(w), 865(m), 815(m), 797(w), 775(m), 553(s), 500(m), 338(m).

Analogous Complexes

The tetrafluorobenzobarrelene and trimethyltetrafluorobenzobarrelene complexes, $[Rh(OMe)(tfb)]_2$ or $[Rh(OMe)(Me_3tfb)]_2$, can be prepared by the same method using $[RhCl(tfb)]_2$[10] and $[RhCl(Me_3tfb)]$,[10] respectively, as starting compounds.

For $[Rh(OMe)(tfb)]_2$: Yield: 94%. *Anal.* Calcd. for $C_{26}H_{18}F_8O_2Rh_2$: C, 43.36; H, 2.52. Found: C, 43.76; H, 2.37. The yellow, air-stable compound is slightly soluble in organic solvents and insoluble in water. It decomposes at 215–220°. IR (Nujol, cm^{-1}): 1649(w), 1489(vs), 1438(s), 1317(s), 1303(s), 1251(w), 1176(s), 1098(s), 1073(m), 1055(vs), 1038(vs), 947(s), 931(w), 914(m), 897(s), 859(s), 844(m), 685(m), 656(w), 489(s), 450(w), 430(s), 416(m), 382(m), 338(m), 290(m).

For $[Rh(OMe)(Me_3tfb)]_2$: Yield 87%. *Anal.* Calcd. for $C_{32}H_{30}F_8O_2Rh_2$: C, 44.80; H, 3.76. Found: C, 45.02; H, 3.85. The yellow, air-stable compound is soluble in dichloromethane and chloroform, slightly soluble in methanol, acetone, hexane, and diethyl ether, and is insoluble in water. It decomposes at 175–185°. ^1H nmr, ($CDCl_3$, TMS, δ): 4.91(m, 2H, $\geqslant$CH), 2.97(m, 4H, $=$CH—), 2.48(br, 12H, $\geqslant$C—Me, OMe), 1.47(s, br, 12H, $\geqslant$C—Me). IR (Nujol, cm^{-1}): 1639(w, br), 1499(s), 1492(s), 1368(m), 1309(m), 1290(m), 1251(m), 1216(w), 1159(m), 1114(m), 1093(m), 1070(vs), 1056(vs), 1043(sh), 1032(sh), 1002(w), 974(s), 929(s), 910(s), 873(w), 852(s), 769(m), 685(m), 653(w), 579(m), 493(m), 370(w), 342(w).

B. BIS(η^4-1,5-CYCLOOCTADIENE)-DI-μ-METHOXYDIIRIDIUM(I).

$$[IrCl(1,5\text{-cod})]_2 + 2\,KOH + 2\,MeOH \longrightarrow [Ir(OMe)(1,5\text{-cod})]_2 + 2\,KCl + 2\,H_2O$$

Procedure

Note. This preparation should be performed with deoxygenated solvents and in an inert atmosphere.

A 100-ml Schlenk flask containing a magnetic stirring bar, and equipped with an argon inlet, is charged with a solution of potassium hydroxide (25 mg, 0.445 mmole) in methanol (5 mL). Addition of a suspension of $[IrCl(1,5\text{-cod})]_2$[11] (149 mg, 0.222 mmole) in methanol (10 mL) turns the color of the initially orange-red suspension to yellow. After being stirred for 30 minutes at room temperature, 40 mL of water are added. The yellow precipitate is collected by filtration, using a fine sintered-glass filter, washed with water (six 5-mL portions), and vacuum-dried over phosphorus(V) oxide. Yield: 124 mg (85%).* *Anal.* Calcd. for $C_{18}H_{30}Ir_2O_2$: C, 32.62; H, 4.56. Found: C, 32.54; H, 4.38.

---

*A yield of 75% was reported by the checkers.

Properties

The yellow, air-stable compound is soluble in chlorinated solvents, and the resulting solutions are air-sensitive. The compound is slightly soluble in methanol, acetone, hexane, benzene, and diethyl ether, and is insoluble in water. It decomposes at 145–165°. The ^1H nmr spectrum ($CDCl_3$, TMS) shows three broad multiplets at $\delta 3.57$ (8H, vinylic protons), 2.22 (8H, allylic protons) and 1.45 (8H, allylic protons), and a sharp singlet at $\delta 3.28$ (6H, methoxide). IR (Nujol, cm^{-1}): 1325(m), 1300(m), 1232(w), 1208(m), 1172(w), 1158(w), 1060(vs), 1005(m), 972(s), 913(m), 894(w), 827(m), 811(w), 783(w), 574(s), 560(sh), 532(m), 512(w), 434(m), 337(m). An X-ray crystallographic study of this complex has been reported.[12]

C. BIS(η^4-1,5-CYCLOOCTADIENE)-DI-μ-HYDROXO-DIRHODIUM(I)

$$[RhCl(1,5\text{-cod})]_2 + 2\ KOH \longrightarrow [Rh(OH)(1,5\text{-cod})]_2 + 2\ KCl$$

Procedure

To a 50-mL round-bottomed flask containing a magnetic stirring bar and charged with a solution of potassium hydroxide (75 mg, 1.337 mmole) in water (4 mL), $[RhCl(1,5\text{-cod})]_2$[9] (320.5 mg, 0.65 mmole) in acetone (35 mL) is added. After being stirred for two hours at room temperature, the yellow suspension is concentrated to ~10 mL in a rotary evaporator. Then 15 mL of water is added. The solid is collected by filtration, using a fine sintered-glass filter, washed with water (ten 5-mL portions), and vacuum-dried over phosphorus(V) oxide. Yield: 280 mg (95%). It can be recrystallized from a mixture of dichloromethane and hexane. *Anal.* Calcd. for $C_{16}H_{26}O_2Rh_2$: C, 42.13; H, 5.74. Found: C, 42.23; H, 5.47.

Properties

The pale-yellow, air-stable solid is soluble in chlorinated solvents, slightly soluble in acetone, hexane, and diethyl ether, and is insoluble in water. It decomposes at 138–145°. MW: Calcd.: 456; Found: 484 (osmometrically in chloroform at 35°). The ^1H nmr spectrum ($CDCl_3$, TMS) shows a broad singlet at $\delta 3.82$ (8H, vinylic protons) and two broad multiplets at $\delta 2.45$ (10H, allylic protons and hydroxide) and 1.67 (8H, allylic protons). The IR (Nujol, cm^{-1}): 3592(s), 3390(m, br). 3300(m,br), 3190(m, br), 1327(m), 1300(w), 1230(w), 1212(m), 1176(w), 1156(w), 1080(w), 998(m), 962(s), 873(sh), 868(m), 817(m), 771(w), 438(m, br), 456(w), 440(w), 397(m), 359(w), 331(w). The ν(OD) in a deuterated sample*: 2628(s), 2501(m, br), 2416(m, br), 2357(m, br).

References

1. J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).
2. R. Usón, L. A. Oro, J. A. Cabeza, and M. Valderrama, *J. Organometal. Chem.*, **231,** C81 (1982).
3. F. Sakurai, H. Suzuki, Y. Moro-oka and T. Ikausa, *J. Am. Chem. Soc.*, **102,** 1749 (1980).
4. G. Pannetier, P. Fougeroux, R. Bonnaire, and N. Platzer, *J. Less-Common Metals*, **24,** 83 (1971).
5. S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 4997 (1965).
6. M. Green, T. A. Kuc and S. H. Taylor, *J. Chem. Soc. (A)*, 2334 (1971).
7. (a) N. Platzer, N. Goasdone, and R. Bonnaire, *J. Organomet. Chem.*, **160,** 455 (1978); (b) S. W. Kaiser, R. B. Saillant, W. M. Butler, and P. G. Rasmussen, *Inorg. Chem.*, **15,** 2681 (1976); (c) B. Denise and G. Pannetier, *J. Organomet. Chem.*, **63,** 423 (1973); (d) R. Usón, L. A. Oro, and J. A. Cuchi, *Rev. Acad. Ciencias Zaragoza*, **31,** 173 (1975); (e) A. C. Sievert and E. L. Muetterties, *Inorg. Chem.*, **20,** 489 (1981).
8. (a) A. Krzywicki and G. Pannetier, *Bull. Soc. Chim. Fr.*, 1093 (1975); (b) D. Brodzki, C. Leclere, B. Denise, and G. Pannetier, *Bull. Soc. Chim. Fr.*, 61 (1976); (c) D. Brodzki, B. Denise, and G. Pannetier, *J. Mol. Catal.*, **2,** 149 (1977); (d) D. Brodzki, B. Denise, R. Bonnaire, G. Pannetier, and C. Leclere, *Fr. Demande*, **2,** 317, 269 (1977); (e) V. A. Kormer, B. D. Babitskii, M. I. Lovach, and N. N. Chesnokova, J. *Polymer, Sci.*, **C16,** 4351 (1969).
9. G. Giordano and R. H. Crabtree, *Inorg. Synth.*, **19,** 218 (1979).
10. D. M. Roe and A. G. Massey, *J. Organomet. Chem.*, **28,** 273 (1971).
11. J. L. Herde, J. C. Lambert, and C. V. Senoff, *Inorg. Syn.*, **15,** 18 (1974).
12. D. Tabrizi and G. Pannetier, *J. Less-Common. Metals*, **23,** 443 (1971).

26. AQUA IONS OF MOLYBDENUM

Submitted by D. T. RICHENS† and A. G. SYKES†
Checked by Z. DORI‡

Molybdenum is at present unique in having aqua ions in five oxidation states. Whereas the complexities of Mo(VI) aqueous solution chemistry have been understood in general terms for some time, it is only in the last 15 years that the aqua ions of the lower oxidation states II through V have been identified, and their structures clearly established. Metal aqua ions are notoriously difficult to crystallize for X-ray diffraction studies, and structures of derivative complexes

---

*Prepared by substituting deuterium oxide for water.

†Department of Inorganic Chemistry, The University, Newcastle-upon-Tyne, NE1 7RU, United Kingdom.

‡Department of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel.