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(Pentamethylcyclopentadienyl)ruthenium compounds. Synthesis and characterization of (.eta.-C5Me5)Ru(CO)2CH2OH

Gregory O. Nelson

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$[Pt_2Me_3(\mu\text{-dppm})_2]$ and chlorine atom abstraction from solvent is necessary to give the observed stoichiometry. The quantum yield for reductive elimination in CH_2Cl_2 solvent is thus 1.0. A methyl exchange between product and IV, which is demonstrated by this reaction, may also be responsible for the apparent intermolecular component of the reductive elimination.[17] The low yields of methane rule out the intermediacy of methyl radicals, while the very high quantum yields are difficult to rationalize in terms of a bimolecular reaction.[18]

Examples are now known in which photolysis of methyl transition-metal complexes may yield homolysis of a methyl-metal bond, ligand dissociation with retention of the metal-alkyl bond[1,19,20] and, in the present case, to reductive elimination by coupling of two methyl groups.

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Registry No. IX, 75583-11-8; $[Pt_2H(\mu\text{-H})Me(\mu\text{-dppm})_2][SbF_6]$, 86802-75-7; $[Pt_2(\mu\text{-H})Me_2(\mu\text{-dppm})_2][PF_6]$, 75862-27-0; $[Pt_2Me_3(\mu\text{-dppm})_2][PF_6]$, 75583-12-9; $[PtMe(py)(dppm)]^+$, 86823-95-2; [PtClMe(dppm)], 76584-41-3; $[Pt_2(\mu\text{-Cl})Me_2(\mu\text{-dppm})_2]^+$, 75862-28-1; pt, 7440-06-4.

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[17] This interpretation is tentative at this stage. Further experiments are needed to determine at which stage the intermolecular reaction occurs.

[18] A bimolecular process, IV* + IV → products, would require that the lifetime of IV* be at least 2.5×10^{-5} s at the concentrations used (4×10^{-4} M) and would give a concentration-dependent quantum yield that was not observed.

[19] Zinnen, H. A.; Pluth, J. J.; Evans, W. J. *J. Chem. Soc., Chem. Commun.* **1980**, 810.

[20] Severson, R,; Wojcicki, A. *J. Organomet. Chem.* **1978**, *157*, 173. Kazlauskas, R. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 1727.

(Pentamethylcyclopentadienyl)ruthenium Compounds. Synthesis and Characterization of (η-C_5Me_5)$Ru(CO)_2CH_2OH$

Gregory O. Nelson

Research Laboratories, Eastman Chemicals Division
Eastman Kodak Company, Kingsport, Tennessee 37662

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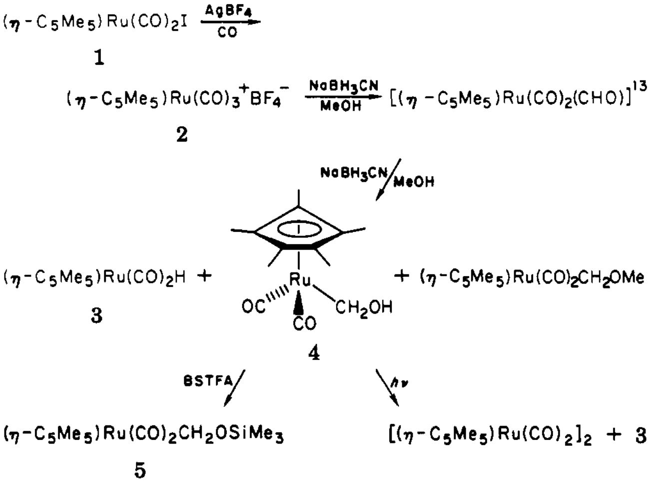
Summary: Reduction of $[(\eta\text{-}C_5Me_5)Ru(CO)_3][BF_4]$ with an excess of $NaBH_3CN$ in methanol gives the hydroxymethyl complex $(\eta\text{-}C_5Me_5)Ru(CO)_2CH_2OH$ (**4**) as the major isolated product. Complex **4** does not undergo carbon monoxide insertion in tetrahydrofuran at 80 °C under 5000 psi of carbon monoxide. Treatment of **4** with *N*,*N*-bis(trimethylsilyl)trifluoroacetamide produces $(\eta\text{-}C_5Me_5)Ru(CO)_2CH_2OSiMe_3$ (**5**).

Transition-metal-bound hydroxymethyl complexes have been repeatedly suggested to be key intermediates in the homogeneous catalyzed reduction of carbon monoxide.[1] Examples of these complexes exist with Re,[2b-d] Os,[2e,f,h] and Ir,[2a] and the reactivities of these systems are being intensively explored. Our interest was in isolating a (hydroxymethyl)ruthenium complex since ruthenium compounds have been shown to catalytically effect carbon monoxide hydrogenation.[3] We describe here our preliminary results in this area including the synthesis and characterization of $(\eta\text{-}C_5Me_5)Ru(CO)_2CH_2OH$ (**4**), the first isolated α-hydroxy complex of ruthenium. While our work was in progress, Graham reported the isolation of the osmium analogue of **4**, $(\eta\text{-}C_5Me_5)Os(CO)_2CH_2OH$.[2h,17]

Scheme I



As reported earlier,[4] heating a solution of $Ru_3(CO)_{12}$ in decane in the presence of an excess of pentamethylcyclopentadiene results in the formation of a near quantitative yield of orange cyrstalline $[(\eta\text{-}C_5Me_5)Ru(CO)_2]_2$. Dissolution of the dimer and a slight excess of iodine in $CHCl_3$ followed by stirring for 2 h at room temperature gives, after a normal workup,[5] bright orange, crystalline $(\eta\text{-}C_5Me_5)Ru(CO)_2I$ (**1**) in 95% yield.[6] As in other cyclopentadienyl systems, the iodide complex proves to be a useful precursor to numerous other derivatives. Treatment of an orange solution of **1** (2 g, 4.8 mmol) in 30 mL of CH_2Cl_2 with $AgBF_4$ (0.93 g, 4.8 mmol) under 60 psi carbon monoxide with stirring for 2 h results in the formation of a gray precipitate and a colorless solution. Filtration followed by addition of diethyl ether precipitates analytically pure $[(\eta\text{-}C_5Me_5)Ru(CO)_3][BF_4]$ (**2**) as a fluffy, white solid in 82% (1.6 g) yield.[7] Complex **2** shows a single peak in the ^1H

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[1] See for instance: Herrmann, W. *Angew Chem., Int. Ed. Engl.* **1982**, 117-130.

[2] (a) Thorn, D. L.; Tulip, T. H. *Organometallics* **1982**, *1*, 1580-1586. (b) Nesmeyanov, A. N.; Anisimov, K. N.; Kolabova, N. E.; Krasnoslobodskaya, L. L. *Izv. Akad. Nauk SSSR, Ser. Khim* **1970**, 860-865; *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1970**, 807-811. (c) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 2811-2815. (d) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Jones, W. D.; Harsey, S. G. *J. Mol. Catal.* 1981, *13*, 43-59 and references therein. (e) Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1982**, *231*, 335-360 and references therein. (f) Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *Ibid.* 1981, *219*, 353-362. (g) The intermediacy of $(\eta\text{-}C_5H_5)Fe(CO)_2CH_2OH$ was proposed in the formation of $(\eta\text{-}C_5H_5)Fe(CO)_2CH_2OCH_3$ via $NaBH_3CN$ reduction of $[(\eta\text{-}C_5H_5)Fe(CO)_3][BF_4]$ in MeOH: Bodnar, T.; Coman, E.; Menard, K.; Cutler, A. *Inorg. Chem.* **1982**, 1275-1277. (h) May, C. J.; Graham, W. A. G. *J. Organomet. Chem.* **1982**, *234*, C49-C51.

[3] Dombeck, D. *J. Am. Chem. Soc.* **1981**, *103*, 6508-6510 and references therein.

[4] King, R. B.; Iqbal, M. Z.; King, A. D., Jr. *J. Organomet. Chem.* **1979**, *171*, 53. Best results are obtained when a 10% excess of C_5Me_5H over $Ru_3(CO)_{12}$ is used in decane heated to 160 °C. After the solution has been heated 15 min, the $Ru_3(CO)_{12}$ solubilizes to form a dark red solution. After the dark red solution is heated for 2 h, pure orange $[(\eta\text{-}C_5Me_5)Ru(CO)_2]_2$ crystallizes out.

[5] The resulting chloroform solution is treated with 15% sodium thiosulfate in water. The crude material obtained from the chloroform is chromatographed on silica gel (toluene) to give pure 1.

[6] Anal. Calcd for $C_{12}H_{15}IO_2Ru$: C, 34.34; H, 3.57. Found: C, 34.24; H, 3.56. 1: IR (CH_2Cl_2) 2030, 1981 cm^{-1}; ^1H NMR (C_6D_6) δ 1.62 (C_5Me_5).

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NMR (CD_2Cl_2) at δ 2.27 and IR peaks [CH_2Cl_2, ν(CO)] at 2110 and 2050 cm^{-1}. Clear colorless crystals of **2** can be obtained by slowly evaporating CH_2Cl_2/Et_2O solutions of cation **2**. These results are summarized in Scheme I.

Recent work has concentrated on the modeling of carbon monoxide hydrogenation by stoichiometric reduction of carbon monoxide on cationic metal centers. This kind of reaction has resulted in the observation of neutral formyl complexes[2c,d,8] and in the isolation of serveral α-hydroxy complexes such as (η-C_5H_5)Re(NO)(CO)CH_2OH[2b–d] and (η-C_5Me_5)Os(CO)$_2CH_2OH$.[2h] All reported reduction techniques[17] that produce hydroxymethyl complexes from coordinated CO [(1) $NaBH_4/THF/H_2O$;[2h] (2) NaH_2AlEt_2;[2d] (3) $NaBH_3CN$, MeOH[2g]] when utilized on [(η-C_5Me_5)Ru(CO)$_3$][BF_4] (**2**) produce (η-C_5Me_5)Ru(CO)$_2CH_2OH$ (**4**) in varying amounts; however, our best results are obtained in methanol with an excess of $NaBH_3CN$ as the reductant. In a typical experiment, [(η-C_5Me_5)Ru(CO)$_3$][BF_4] (0.50 g, 1.2 mmol) is added to a −50 °C solution of $NaBH_3CN$ (0.225 g, 3.6 mmol) in 20 mL of degassed MeOH. The resulting mixture is allowed to warm to room temperature. Then the mixture is stirred for 2 h, the methanol is stripped, and the residue is extracted with pentane (2 × 15 mL). After removal of solvent, a mixture of (η-C_5Me_5)Ru(CO)$_2$H (**3**),[9] (η-C_5Me_5)Ru(CO)$_2CH_2OCH_3$,[10] and (η-C_5Me_5)Ru(CO)$_2CH_2OH$ (**4**) remains. Pure, white, crystalline **4** (0.24 g, 60%) is afforded by recrystallization of the crude material from pentane at −78 °C: IR [C_6H_6, ν(CO)] 1997, 1932 cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.96 (d, J = 6 Hz, CH_2, 2 H), 1.68 (s, C_5Me_5, 15 H), 0.88 (t, J = 6 Hz, OH, 1 H).[12] An excess of $NaBH_3CN$ is required since the use of 1 mol equiv of reductant yields (η-C_5Me_5)Ru(CO)$_2CH_2OCH_3$ as the major isolated product. The reason for this behavior is not yet known.[13] Initial work with **4** indicates that it is not as robust as its osmium analogue.[2h] Analytically pure crystals of **4** turn dark after several hours of exposure to air; pentane solutions turn dark after several minutes of exposure to air. IR and ^{1}H NMR show that mixtures containing (η-C_5Me_5)Ru(CO)$_2$H and [(η-C_5Me_5)Ru(CO)$_2$]$_2$ are formed.[15]

That the decomposition is not related to thermal stability is evident because benzene-d_6 solutions of **4**, after being heated at 85 °C for several hours in the absence of air, do not show a significant loss of the α-hydroxy complex. However, at 127 °C (toluene-d_8) **4** undergoes a first-order decomposition which can be followed by ^{1}H NMR ($k = 2.9 \times 10^{-3}$ s^{-1}, $\Delta G^{\ddagger}_{400} = 28.3$ kcal mol^{-1}). This can be compared with (η-C_5Me_5)Os(CO)CH_2OH that decomposes at 174 °C with a first-order rate constant of 9.0×10^{-5} s^{-1} ($\Delta G^{\ddagger}_{447} = 34.8$ kcal mol^{-1}).[2h]

One of the key steps proposed in the formation of C_2 oxygenates with transition-metal catalysts is migration of an α-hydroxymethyl group to coordinate carbon monoxide. It is, therefore, of interest that not one of the isolated α-hydroxymethyl complexes has been reported to undergo carbon monoxide insertion. Complex **4** is thus far not unusual in this aspect. A THF solution of **4** heated to 80 °C under 5000 psi of carbon monoxide for 5 h results only in recovery of the starting compound. More intense thermal, as well as oxidative, conditions are being probed to attempt to induce CO insertion in **4** and other related ruthenium complexes.

One derivative of **4** has been synthesized. Treatment of crude reaction mixtures containing **4** with *N,N*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) results, after a normal workup, in the isolation of (η-C_5Me_5)Ru(CO)$_2CH_2OSiMe_3$ (**5**) as colorless air- and water-sensitive crystals.[16] Complex **5** exhibits ^{1}H NMR signals (C_6D_6) at δ 4.87 (s, CH_2, 2 H), 1.65 (s, C_5Me_5, 15 H), and 0.21 (s, $SiMe_3$, 9 H) and IR [CH_2Cl_2, ν(CO)] at 1995 and 1935 cm^{-1}. This is a convenient derivative because it can be easily purified by column chromatography; unfortunately, we have been unable to regenerate **4** from the trimethylsilyl complex. Treatment of **5** with either tetrabutylammonium fluoride or the milder ammonium bifluoride[2a] results only in isolation of (η-C_5Me_5)Ru(CO)$_2$H in high yield.

In summary, several derivatives of the (η-C_5Me_5)Ru(CO)$_2$ group including the hydroxymethyl complex (η-C_5Me_5)Ru(CO)$_2CH_2OH$, which is obtained by reduction of [(η-C_5Me_5)Ru(CO)$_3$][BF_4], have been isolated. Further studies are directed toward modeling carbon monoxide hydrogenation with (pentamethylcyclopentadienyl)ruthenium dicarbonyl complexes.[13]

Acknowledgment. The author thanks Dr. S. W. Polichnowski for many helpful discussions and Eastman Chemicals Division for allowing the publication of this work.

Registry No. 1, 86862-65-9; 2, 86853-54-5; 3, 82728-97-0; 4, 86853-55-6; 5, 86853-56-7; (η-C_5Me_5)Ru(CO)$_2CH_2OCH_3$, 86853-57-8; $Ru_3(CO)_{12}$, 15243-33-1; [(η-C_5Me_5)Ru(CO)$_2$]$_2$, 70669-56-6; BSTFA, 21149-38-2.

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[7] Anal. Calcd for $C_{13}H_{15}O_3RuBF_4$: C, 38.28; H, 3.68. Found: C, 38.40; H, 3.68.

[8] Wilson, T.; Lin, G.; Wong, W.; Kiel, W.; Wong, V.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141–152 and references therein.

[9] Hydride complex **3** is isolated as very air-sensitive colorless crystals and has thus far been identified by IR and NMR only: IR (C_6H_6) 2000, 1941 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.72 (s, C_5Me_5), −10.20 (s, Ru–H). **3** readily decomposes to [(η-C_5Me_5)Ru(CO)$_2$]$_2$ when exposed to air or to light.

[10] This compound is identified by the similarity of its IR and ^{1}H NMR to (η-C_5H_5)Ru(CO)$_2CH_2OCH_3$.[11] (η-C_5Me_5)Ru(CO)$_2CH_2OCH_3$-(CH_2Cl_2): IR 2000, 1935 cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.60 (s, CH_2), 3.28 (s, CH_3), 1.65 (s, C_5Me_5).

[11] Moss, J. R.; Pelling, S. *J. Organomet. Chem.* **1982**, *236*, 221–227.

[12] Anal. Calcd for $C_{13}H_{18}O_3Ru$: C, 48.23; H, 5.56. Found: C, 48.34; H, 5.60.

[13] This behavior is possibly related to the chemistry of the assumed intermediate formyl complex (η-C_5Me_5)Ru(CO)$_2$(CHO). We have recently generated this complex by interaction of [Ph_3PCuH]$_6$[14] with **2**. The formyl complex: IR (THF) 2015, 1964, 1645 cm^{-1}; ^{1}H NMR (C_6D_6) δ 14.0 (s, CHO), 1.5 (s, C_5Me_5). Surprisingly this complex only very slowly decomposes to **3** at room temperature in solution. The chemistry of this complex is being explored; details will be reported later; Sumner, C.; Nelson, G., in preparation.

[14] Churchill, M. R.; Bezman, S. A.; Osborn, J. A.; Wormald, J. *Inorg. Chem.* **1972**, *11*, 1818.

[15] Photolysis of **4** in benzene-d_6 also produces mixtures of **3** and [(η-C_5Me_5)Ru(CO)$_2$]$_2$. This reaction is similar to that observed with the osmium analogue[2h] except no [(η-C_5Me_5)Os(CO)$_2$]$_2$ is observed in that case, probably because (η-C_5Me_5)Os(CO)$_2$H is more stable than **3**.

[16] Complex **5** is usually obtained as an oil that slowly crystallizes when stored at 7 °C. Anal. Calcd for $C_{16}H_{26}O_3RuSi$: C, 48.54; H, 6.58. Found: C, 48.58; H, 6.54.

[17] After this manuscript was submitted, a copy of the journal containing Astruc's report of (μ-C_5Me_5)Fe(CO)$_2CH_2OH$ was received in our library: Lapinte, C.; Astruc, D. *J. Chem. Soc., Chem. Commun.* 1983, 430.

Sterically Induced η^2-Acyl Formation: Syntheses and Structures of $TpMo(CO)_2(\eta^2\text{-}COR)$ (R = Me, Ph) and $TpMo(CO)_3Br$ (Tp = Hydridotris(pyrazolyl)borate)

M. David Curtis,* Kom-Bei Shiu, and William M. Butler

Department of Chemistry, The University of Michigan
Ann Arbor, Michigan 48109

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Summary: The anion $TpMo(CO)_3^-$ (Tp = hydridotris(pyrazolyl)borate) reacts with MeI or Me_3OBF_4 or with