This concept was supported by comparison of [CpFe(CO)$_2$]$_2$ with [Cp*Fe(CO)$_2$]$_2$ that showed a shift in binding energy of 0.4 eV on methyl substitution of the single Cp ligand.

For the series of compounds listed in Table I, average changes of 0.4 eV occurred for substitution of each C_5H_5 unit by a $C_5(CH_3)_5$ group. Feltham and Brant have noted that a one-electron oxidation of a transition metal results in a shift of approximately 1 eV to higher binding energy.[10] For the bis(cyclopentadienyl) complexes listed in Table I, we observed shifts of 0.8 eV (18.5 kcal/mol) on complete methyl substitution. Thus, *the substitution of two Cp* ligands for Cp ligands has an electronic effect approaching that of a one-electron reduction of the metal.*

Since the electrochemical oxidation of ferrocene to the ferrocenium ion has been thoroughly investigated,[11] it was of interest to compare the effect of methyl substitution on the ease of removing a valence electron from iron[12] vs. the ease of removal of an inner-shell electron. In general, this electrochemical data (Table I) supported our contention that methyl substitution on the cyclopentadienyl moiety has a dramatic electronic effect, which results in a systematic lowering of the $E^{\circ\prime}$ (or $E_{1/2}$). For the iron complexes listed in Table I, the substitution of five hydrogens by five methyl groups resulted in an average change of 0.3V in the $E^{\circ\prime}$ for the oxidation of iron. The titanocenes, zirconocenes, and hafnocenes presented a more difficult situation. Since the HOMO of these complexes cannot be associated with the metal atom,[6c,d] oxidation must involve one of the ligands. In contrast to the suggestion that titanocene dichloride has its HOMO associated with chloride,[6c] our electrochemical studies suggest that the HOMO is Cp based. The similarities in $E_{1/2}$ for the titanocene fluorides, chlorides, and bromides was diagnostic of oxidation of the Cp or Cp* moiety.[13,14]

In summary, we have shown that methyl substitution on the cyclopentadienyl group has a major influence on the electronic characteristics of metals that are complexed to this widely used ligand.

Acknowledgment. We are indebted to the National Science Foundation for a grant that partially supported this investigation.

Registry No. Cp$_2$TiF$_2$, 309-89-7; CpCp*TiF$_2$, 38496-78-5; Cp*$_2$TiF$_2$, 87050-22-4; Cp$_2$TiCl$_2$, 1271-19-8; CpCp*TiCl$_2$, 38496-87-6; Cp*$_2$TiCl$_2$, 11136-36-0; Cp$_2$TiBr$_2$, 1293-73-8; CpCp*TiBr$_2$, 87050-23-5; Cp*TiBr$_2$, 87050-24-6; Cp$_2$ZrCl$_2$, 1291-32-3; CpCp*ZrCl$_2$, 81476-73-5; Cp*$_2$ZrCl$_2$, 54039-38-2; Cp$_2$HfCl$_2$, 12116-66-4; CpCp*HfCl$_2$, 87050-25-7; Cp*$_2$HfCl$_2$, 85959-83-7; Cp$_2$Fe, 102-54-5; CpCp*Fe, 83928-47-6; Cp*$_2$Fe, 12126-50-0; [CpFe(CO)$_2$]$_2$, 12154-95-9; [Cp*Fe(CO)$_2$]$_2$, 35344-11-7.

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[10] Feltham, R. D.; Brant, P. *J. Am. Chem. Soc.* **1982**, *104*, 641.

[11] Slocum, D. W.; Ernst, C. R. *Adv. Organomet. Chem.* **1972**, *10*, 79. Kuwana, T.; Bublitz, D. E.; Hoh, G. *J. Am. Chem. Soc.* **1960**, *82*, 5811. Mason, J. G.; Rosenblum, M. *Ibid.* **1960**, *82*, 4206. Hoh, G. L. K.; McEwen, W. E.; Kleinberg, J. *Ibid.* **1961**, *83*, 3949. Little, W. F.; Eisenthal, R. *Ibid.* **1961**, *83*, 4936. Gubin, S. P.; Perevalova, E. G. *Dokl. Akad. Nauk SSSR* **1962**, *143*, 1351. Hall, D. W.; Russell, C. D. *J. Am. Chem. Soc.* **1967**, *89*, 2316. Sabattini, M. M.; Cesarotti, E. *Inorg. Chim. Acta* **1977**, *24*, L9. Grimes, H.; Logan, S. R.; *Ibid.* **1980**, *45*, L223. Deeming, A. J. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W.; Eds.; Pergamon Press: New York, 1982; Vol. 4, p 480. Kotz, J. C.; Vining, W.; Coco, W.; Rosen, R.; Dias, A. R.; Garcia, M. H. *Organometallics* **1983**, *2*, 68.

[12] The oxidation of Cp*$_2$Fe in molten AlCl$_3$/1-butylpyridinium chloride occurred 0.53 V more readily than the oxidation of Cp$_2$Fe. Gale, R. J.; Singh, P.; Job, R. *J. Organomet. Chem.* **1980**, *199*, C44. Their difference compares quite well with our difference of 0.54V measured in methylene chloride.

[13] This is consistent with recent studies of this system by Green and co-workers.[6d]

[14] The observation that the fluorides oxidized more easily than the corresponding chlorides or bromides was particularly interesting. We wish to speculate that in the titanocene difluorides the Cp (or Cp*) ligand is more ionic than in the analogous chlorides and bromides. As the ionic character of the Cp (or Cp*) ring increases, it becomes more easily oxidized to the corresponding radical. For comparison, we have shown that lithium pentamethylcyclopentadienide has an $E_{1/2}$ of −0.56 V and lithium cyclopentadienide[15] has an $E_{1/2}$ of −0.44 V in 90:10 THF–HMPA at −30 °C at a platinum electrode. The scan rate was 100 mV/s. This data supported our contention that the ease of oxidation of the cyclopentadienide system was a function of the ionic character of this species.

[15] For an earlier report of the $E_{1/2}$ of lithium cyclopentadienide ($E_{1/2}$ = −0.37 V) in 83:17 THF–HMPA at −60 °C at a carbon electrode see: Juan, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741.

Photochemically Induced Reductive Elimination of Ethane from a Binuclear Methylplatinum Complex†

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Summary: Photolysis (362 ± 7 nm) of [Pt$_2$Me$_3$(μ-dppm)$_2$][PF$_6$], dppm = Ph$_2$PCH$_2$PPh$_2$, in pyridine leads to fragmentation to [PtMe$_2$(dppm)] and [PtMe(py)(dppm)][PF$_6$] (Φ = 0.6), but in MeCN (Φ = 0.1), acetone (Φ = 1.2 ± 0.3), or CH$_2$Cl$_2$ (Φ = 2.0 ± 0.1) photolysis gives a new reaction involving reductive elimination of ethane, followed by further reactions dependent on the solvent. Reductive elimination is at least partially intramolecular as shown by labeling studies.

There are reports of reductive elimination of H_2 from complexes [L$_n$MH$_2$] and of CH_4 from [L$_n$MMeH] using both thermal and photochemical activation[1,2] but, though thermal reductive elimination of ethane from [L$_n$MMe$_2$] is well-known,[2] no similar photochemical reductive elimination involving C–C bond formation has been established.[1,3] We wish to report an example of this type of reaction involving a binuclear methylplatinum complex.

Photolysis of complexes I–III in pyridine or acetonitrile occurred according to eq 1,[6,7] and quantum yields (Table

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† Publication No. 298 from the photochemistry unit, University of Western Ontario

[1] Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry", Academic Press: New York, 1979.

[2] Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978.

[3] The closest analogy may be the coupling of aryl groups on photolysis of [Ti(C$_6$H$_4$Me)$_2$(η-C$_5$H$_5$)$_2$],[4] but mechanistic studies have not been reported.[1] Several systems are known to give coupling of alkyl groups in low yield.[5]

[4] Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189.

[5] Ozawa, F.; Yamamoto, A.; Ikariya, T.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1481. Perkins, D. C. L.; Puddephatt, R. J.; Tipper, C. F. H. *J. Organomet. Chem.* **1979**, *166*, 261.

[6] Hill, R. H.; de Mayo, P.; Puddephatt, R. J. *Inorg. Chem.* **1982**, *21*, 3642. Geoffroy and co-workers report a quantum yield of 0.62 at 366 nm for photolysis of I in MeCN. Foley, H. C.; Morris, R. H.; Targos, T. S.; Geoffroy, G L. *J. Am. Chem. Soc.* **1981**, *103*, 7337.

[7] Brown, M. P.; Cooper, S. J.; Frew, A. A.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J.; Thomson, M. A. *J. Chem. Soc., Dalton Trans.* **1982**, 299.

[8] Platinum-containing products were idetified by monitoring the course of photolysis by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy and were then isolated and characterized as described previously.[6,7,9] Volatile hydrocarbon products were determined by GC using 5A molecular sieve or Porapak Q columns and were within 20% of the values expected from the stoichiometry.

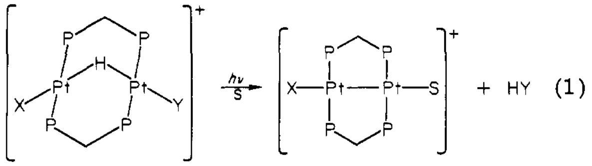
[9] Azam, K. A.; Puddephatt, R. J.; Brown, M. P.; Yavari, A. *J. Organomet. Chem.* **1982**, *234*, C31.

Table I. Quantum Yields (362 ± 7 nm) for Photolysis of Diplatinum Complexes[a]

complex	quantum yield py	quantum yield MeCN	ref
$[Pt_2H_2(\mu\text{-}H)(\mu\text{-dppm})_2][PF_6]$	0.57	0.81	6
$[Pt_2H(\mu\text{-}H)Me(\mu\text{-dppm})_2][SbF_6]$	0.21	0.37	this work
$[Pt_2(\mu\text{-}H)Me_2(\mu\text{-dppm})_2][PF_6]$	0.30	0.34	this work
$[Pt_2Me_3(\mu\text{-dppm})_2][PF_6]$	0.6	0.1	this work

[a] Quantum yields were determined by using a Jasco spectroirradiator. The experimental method and analysis method were as described previously.[6] Ferrioxalate actinometry was used for calibration. All quantum yields are measured for disappearance of reagent and are estimated to be accurate to ±20% and are precise to ±10%.

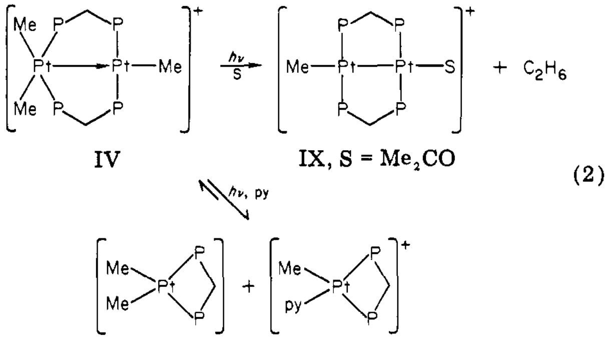
I) were higher in acetonitrile than in pyridine. Complex II yielded H_2 rather than CH_4, and III yielded CH_4 rather than C_2H_6 on reductive elimination.



I, X = Y = H
II, X = Me, Y = H
III, X = Y = Me

V, X = H, S = py
VI, X = H, S = MeCN
VII, X = Me, S = py
VIII, X = Me, S = MeCN

In contrast to the above, the quantum yield for photolysis of IV[10] was considerably higher in pyridine than in acetonitrile (Table I), and different reactions were observed. Thus, photolysis in pyridine gave largely a mixture of mononuclear products $[PtMe_2(dppm)]$ and $[PtMe(py)(dppm)]^+$, eq 2,[11] and no ethane was evolved at this stage, whereas photolysis in acetonitrile gave ethane. In acetone, photolysis occurred cleanly up to 75% of reaction to give IX and ethane (1.0 mol) with a quantum yield of 1.2 ± 0.3, though the reaction could not be taken to completion due to photolysis of product in the late stages.[12] Ethane was also evolved with high quantum yield on photolysis in benzene, but precipitation of product caused complications. A clean reaction (Figure 1) occurred in dichloromethane solution to give $[Pt_2Me_2(\mu\text{-}Cl)(\mu\text{-dppm})_2]^+$,[13] and 0.5 mol of ethane[8] for each mole of IV decomposed, and an accurate quantum yield of 2.0 ± 0.1 was measured for photodecomposition of IV.



IV

IX, S = Me_2CO

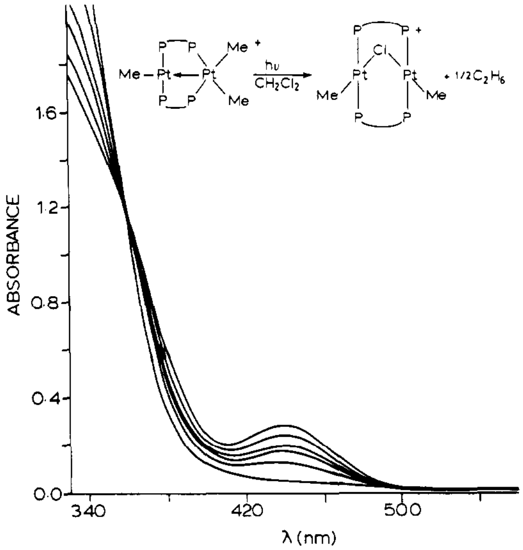


Figure 1. Changes in absorption spectra on photolysis of $[Pt_2Me_3(\mu\text{-dppm})_2][PF_6]$ in CH_2Cl_2. Absorbance at 450 nm decreases on photolysis.

To determine if reductive elimination was intramolecular, a 1:1 mixture of $[Pt_2Me_3(\mu\text{-dppm})_2][PF_6]$ and $[Pt_2(CD_3)_3(\mu\text{-dppm})_2][PF_6]$ was photolyzed and the ratio of $C_2D_6/C_2H_3D_3$ produced was measured by mass spectrometry.[14] For photolyses in CH_2Cl_2 and acetone this ratio was 1:0.4 and 1:1.0, respectively, whereas a ratio of 1:0 and 1:2 would be expected for intramolecular or intermolecular eliminations, respectively. The experiment shows clearly that at least part of the reaction is intramolecular.

The above observations are interpreted in the following way. Excitation of IV probably occurs by a d → σ^*(PtPt) transition that leads to cleavage of the donor-acceptor Pt→Pt bond.[15] The good donor pyridine can then coordinate to the monomethylplatinum center and cleavage of the dimer to mononuclear fragments follows, with no ethane elimination. Acetonitrile appears to be a strong enough ligand for platinum to coordinate reversibly and hence deactivate the excited state but does not lead to fragmentation to mononuclear complexes. The result is a low quantum yield for reductive elimination. In the weak donor solvents acetone, benzene and dichloromethane, reductive elimination of ethane from the excited state is very efficient and we assume that this gives the coordinatively unsaturated $[Pt_2Me(\mu\text{-dppm})_2]^+$. We cannot tell if the elimination occurs at a single platinum center or by a binuclear process.[16] In acetone, the product is trapped as the acetone complex (eq 2), but in dichloromethane a further rapid thermal reaction with a second molecule of

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[10] Brown, M. P.; Cooper, S. J.; Frew, A. A.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R.; Thomson, M. A. *Inorg. Chem.* **1981**, *20*, 1500.

[11] The compounds were identified by the ^1H and $^{31}P\{^1H\}$ NMR spectra by comparison with authentic samples but were not separated. Authentic $[PtMe(py)(dppm)]^+$ was prepared by chloride abstraction from $[PtClMe(dppm)]$ or from $[Pt_2(\mu\text{-}Cl)Me_2(\mu\text{-dppm})_2]^+$ in methanol by using $AgNO_3$, followed by addition of pyridine [δ 1.02 (m, $^3J(PH)$ cis 3, $^3J(PH)$ trans 8, $^2J(PtH)$ = 61 Hz, *Me*Pt), -42.3 ($^1J(PtP)$ = 3380 Hz), and -26.6 ($^1J(PtP)$ = 1270 Hz, $^2J(PP)$ = 38 Hz, Pt*P* trans to py and Me, respectively)].

[12] This is the reason for the large uncertainty in the quantum yield. The product IX, was identified by its ^1H NMR spectrum [δ(MePt) 0.29 ($^3J(PH)$ = 7.5 Hz, $^2J(PtH)$ = 70 Hz)] and by conversion to the more stable derivative VII on reaction with pyridine.

[13] Cooper, S. J.; Brown, M. P.; Puddephatt, R. J. *Inorg. Chem.* **1981**, *20*, 1374.

[14] Using a Varian MAT 311 spectrometer, with 25 eV ionizing voltage. Mole ratios were determined by peak heights at *m/e* 36 and 33 after correction for background. The yields of C_2H_6 under these conditions could not be determined accurately, due to interference from solvent and from fragmentation of C_2D_6, and are not quoted. The concentration of each reagent was 3×10^{-3} M.

[15] For a discussion of electronic energy levels in related molecules see: Hoffman, D. M.; Hoffmann, R. *Inorg. Chem.* **1981**, *20*, 3543.

[16] We note that mononuclear complexes $[PtMe_2L_2]$ are not photosensitive except in solvents such as $CHCl_3$ or CCl_4.

$[Pt_2Me_3(\mu\text{-dppm})_2]$ 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.

Acknowledgment. We thank NSERC (Canada) for financial support and Dr. P. de Mayo for access to the Jasco spectroirradiator used in the quantum yield determinations and for valuable discussions.

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 $(\eta\text{-}C_5Me_5)Ru(CO)_2CH_2OH$

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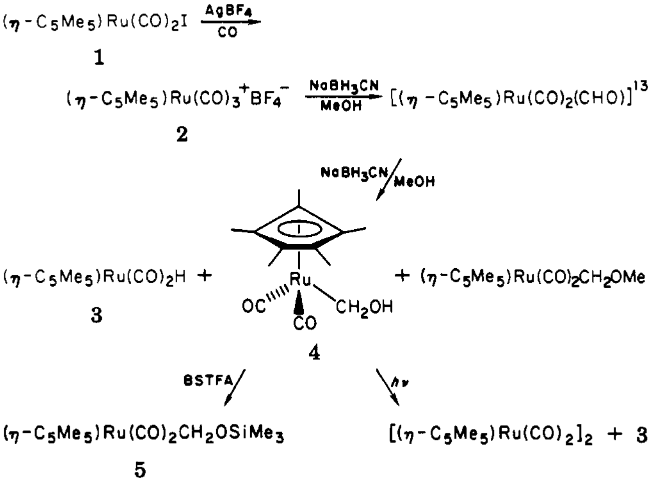
Summary: Reduction of $[(\eta\text{-}C_5Me_5)Ru(CO)_3][BF_4]$ with an excess of $NaBH_3CN$ in methanol gives the hydroxymethyl complex $(\eta\text{-}C_5Me_5)Ru(CO)_2CH_2OH$ (**4**) as the major isolated product. Complex **4** does not undergo carbon monoxide insertion in tetrahydrofuran at 80 °C under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