The resulting mixture of alcohols (~8:1 (T/C) at the newly created ring junction) was directly subjected to successive oxidations, initially of the secondary hydroxyl group to the related ketone (with simultaneous removal of the ethoxyethyl group),[18] followed by exposure to excess Jones reagent[19] which resulted in oxidation to the derived keto aldehyde, concomitant aldol cyclization, and further oxidation to afford after esterification the tricyclic diketone **14** in 45% overall yield (chromatographically purified) from **12**. The structure and stereochemistry assigned to **12** was confirmed by single-crystal X-ray analysis of lactone **15** derived from **14** (Scheme I).[20] Creation of the eight-membered ring was then initiated by reduction of the more accessible carbonyl group in **14** to the required equatorial alcohol, deprotection of the remaining hydroxyl, and conversion to the bismesylate **16** (mp 122–124 °C) in standard fashion in 43% overall yield from **12** (Scheme I). Selective elimination of the primary mesylate provided the unsaturated mesylate **17** (58% yield, 76% conversion) possessing the requisite antiperiplanar geometry suitable for fragmentation.[21]

Exposure of **17** to excess $NaOCH_3$ in CH_3OH at reflux smoothly effected the desired cleavage to afford **18** in 73% yield (Scheme II). Closure of the final ring was then accomplished by Dieckman condensation, and immediate decarboxylation provided the crystalline ketone **19** (mp 55–57 °C) in 76% yield.

With the ring skeleton assembly complete, the final task was introduction of the eight carbon side chain of **1** which was initiated by conversion of ketone **19** via the intermediate lithium enolate, under Saegusa conditions, to the key tricyclic enone **20** in 55% yield (65% conversion).[22]

A variety of strategies were investigated to permit introduction of a suitably protected intact side chain with good stereocontrol over both sites of attachment (C_{14}) and the acyclic stereocenter (C_{15}).[20] However, high levels of stereocontrol have thus far been achieved only over C_{14}. Reaction of **20** with the mixed cuprate **21** derived from the suitably protected intact side chain gave an inseparable mixture of ketones **22** (~1:1) in 70% yield.[23] Fortunately, treatment of ketones **22** with $TsNHNH_2$ catalyzed by $(COOH)_2$ afforded a separable mixture (prep TLC) of the derived tosyl hydrazones **23** (more polar) and **24** in 86% yield.[24] Reduction of **23** with $ZnCl_2ONaCNBH_3$ in CH_3OH at 90 °C (sealed system) afforded (±)-ceroplastol I (**1**) (~50%) identical by spectroscopic (300 and 500 MHz NMR) and TLC (several solvent systems) comparison with the an authentic sample of natural (+)-**1**.[25,26] Subsequent conversion of (±)-**1** to the derived 3,5-dinitrobenzoate **25** and spectroscopic (300 and 500 MHz NMR), TLC, and HPLC comparison with a sample of (+)-**25** derived from natural material further confirmed their identity.

Further studies are currently underway whose goal is to devise a strategy which also will permit control over the acyclic C_{15} center. The foregoing sequence, which also constitutes formal total syntheses of ceroplastol II (**2**) and albolic acid (**3**), affords (±)-**1** in 22 steps (from **5**) and is readily adaptable to preparation of (+)-ceroplastol I.[12]

Acknowledgment. We are extremely grateful to the Institute of General Medical Sciences (NIGMS) of the National Institutes of Health for a grant (GM-29290) in support of these studies. We also thank Drs. S. D. Arthur and P. C. Naegely for their valuable contributions to the early stages of these studies.

Supplementary Material Available: Spectroscopic and selected analytical data for compounds **1**, **7**, **8**, **10**, **12**, **14**–**20**, **22**, and **23** (14 pages). Ordering information is given on any current masthead page.

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(19) Eisenbraun, E. *Organic Synthesis*; Wiley: New York, 1973; Collect. Vol. 5, p 310.

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(23) The mixed cuprate **21** was readily prepared from (*E*)-1-hydroxy-2-methyl-2-hepten-6-one[27] by the following sequence: (a) TBSCl, imidazole, DMF, 25 °C, 10 h (79%); (b) $NaBH_4$, C_2H_5OH, 0 °C, 0.5 h (80%); (c) Ph_3P (2 equiv), CCl_4, Δ, 2 h (82%); (d) $Li^+(4\text{-}t\text{-BuPh})_2^{\bullet-}$ (2 equiv), THF, −78 °C, 0.25 h, then added to $nC_3H_7C{\equiv}CCu$ (1 equiv) precomplexed with HMPT (2 equiv) at 25 °C, Et_2O, −23 °C, 3 min.[28]

(24) The stereochemistry at C_{14} and C_{15} in hydrazones **23** and **24** was assigned after reduction. Only **23** afforded (±)-**1**; however, the similarity of the NMR spectra of the diastereomer of ceroplastol I obtained from **24** strongly suggests that **23** and **24** are epimeric only at C_{15}.

(25) Kim, S.; Oh, C. H.; Ko, J. S.; Ahn, K. H.; Kim, Y. J. *J. Org. Chem.* **1985**, *50*, 1927.

(26) We are grateful to Drs. Shuyen and Ian Harrison for supplying us with a generous sample of natural (+)-ceroplastol I 3,5-dinitrobenzoate for comparison with our synthetic materials. Natural (+)-ceroplastol I was obtained by cleavage of the 3,5-dinitrobenzoate.

(27) Taylor, W. G. *J. Org. Chem.* **1979**, *44*, 1020.

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In Situ FTIR Spectroscopy at Elevated CO Pressure. Evidence for Single-Electron Transfer in the Catalytic Carbonylation of Nitroaromatics

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Much effort has been expended to develop alternative preparations of aryl isocyanates which avoid utilizing phosgene.[1] The focus of much work has been directed toward discovering a direct carbonylation of the nitro functionality to the isocyanate or carbamate[1-3] (eq 1). One of the most effective catalysts found

$$ArNO_2 + 3CO + CH_3OH \xrightarrow{cat.} ArNHC(O)OCH_3 + 2CO_2 \qquad (1)$$

in eq 1 was $Ru(dppe)(CO)_3$ (dppe = 1,2-bis(diphenylphosphino)ethane).[3] We report here our studies on the deoxygenation steps in the mechanism of this reaction which suggest that activation of the nitro group occurs via a one-electron reduction by the Ru(0) complex.

The principal products under typical catalytic reaction conditions[4] using nitrotoluene were *p*-tolylmethylcarbamate and *p*-toluidine. Small amounts of formylidene-*p*-toluidine arising from the condensation of *p*-toluidine and formaldehyde were observed. Insight into the mechanism of the reaction was obtained by in situ examination of the working catalyst solutions using FTIR spectroscopy. The high-pressure CIR reactor has been described elsewhere[5,6] and is commercially available. Figure 1a shows that immediately after mixing all of the reagents with the catalyst the three absorptions at 2003, 1934, and 1912 cm^{-1} are attributable to the unchanged complex. After the solution was allowed to stand for 3 h under CO pressure, three new absorptions at 2058, 1982,

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(1) Cenini, S.; Pizzotti, M.; Crotti, C. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; Reidel: Dordrecht: 1988; Vol. 6, pp 97–198.

(2) (a) Cenini, S.; Pizzotti, M.; Crotti, C.; Porta, F.; La Monica, G. *J. Chem. Soc., Chem. Commun.* **1984**, 1286–1287. (b) Cenini, S.; Crotti, C.; Pizzotti, M.; Porta, F. *J. Org. Chem.* **1987**, *53*, 1243–1250.

(3) Grate, J. H.; Hamm, D. R.; Valentine, D. H. (a) U.S. Patent 4,600,793, 1986. (b) U.S. Patent 4,603,216, 1986. (c) U.S. Patent 4,629,804, 1986. (d) U.S. Patent 4,705,883, 1987.

(4) Typical conditions for the catalysis were 3 mM catalyst, 100 mM *p*-nitrotoluene, 40 mM methanol, a total volume of 15 mL, a temperature of 145 °C, and a pressure of CO of 83 atm. The composition of the starting solution differed in two aspects from the original reports.[3a,b,d] First, a solvent mixture of benzene and methanol (compared to neat methanol in the patent) was used to increase the solubility of the catalyst at lower temperatures. Second, the aryl amine was left out of the system.[3c]

(5) Moser, W. R.; Cnossen, J. E.; Wang, A. W.; Krouse, S. A. *J. Catal.* **1985**, *95*, 21–32.

(6) Darensbourg, D. J.; Gibson, G. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; pp 230–248.

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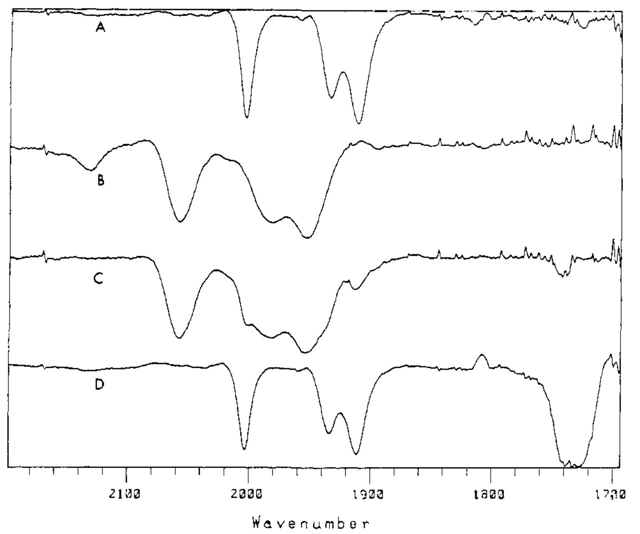


Figure 1. In situ IR spectra of a catalytically active solution at 85 atm CO in benzene/MeOH: (a) immediately following mixing of all reagents at room temperature, (b) spectrum after solution has reacted at 34 atm for 3 h at room temperature, (c) after heating to 100 °C, and (d) spectrum obtained after cooling to 85 °C the reaction that ran at 135 °C for 1.5 h. The CO pressure at 135 °C was 41 atm. The peak at 2130 cm^{-1} in b is due to dissolved CO.

and 1954 cm^{-1} appeared (Figure 1b). As the solution was heated the carbamate was produced as indicated by the absorption at 1740 cm^{-1}, and, upon consumption of the nitrotoluene, the absorptions due to Ru(dppe)(CO)$_3$ reappear. The final spectrum shows that the starting catalyst was not only qualitatively but quantitatively recovered.

The shift of the same three-band pattern to higher energy suggested that the Ru(dppe)(CO)$_3$ was oxidized. For comparison, *trans*-[Fe(PPh$_3$)$_2$(CO)$_3$]PF$_6$ exhibits[7] one ν_{CO} at 1999 cm^{-1}. Solutions removed during the early stages of reaction were found to have a greenish-brown color. These facts suggested that one-electron oxidation of Ru(dppe)(CO)$_3$ by the nitroaromatic might be occurring. Precedent exists for the single electron oxidation of metals by nitroaromatics[1] especially in the work of Berman and Kochi[8] on the reaction of Ni(PR$_3$)$_4$ with nitrobenzene to give Ni(PR$_3$)$_2$(PhNO), PR$_3$, and OPR$_3$.

A study of the stoichiometric reactions of Ru(dppe)(CO)$_3$ with nitro- and nitrosoaromatics *at room temperature* using quantitative GC analysis established that CO$_2$ formation (1.0 equiv) and CO consumption (1.0 equiv) was rapid using *p*-chloronitrobenzene ($t_{1/2}$ = 10 m). The rate of the second CO$_2$ loss was much slower ($t_{1/2}$ = 150 m) and was paralleled by the rate of CO$_2$ loss when *p*-chloronitrosobenzene was reacted with Ru(dppe)(CO)$_3$.

Infrared spectroscopy (Figure 2a) indicated that the consumption of Ru(dppe)(CO)$_3$ corresponded to the rate of the first deoxygenation. The intermediate exhibited two bands at 2051 and 1971 cm^{-1} indicative of a reduction of the electron density on the metal, but it was not the same pattern observed at high pressures of CO. As the second CO$_2$ was lost, the spectrum gradually changes (Figure 2b). During these reactions no carbamate or aromatic amine was formed, suggesting the ArN moiety remained attached to the Ru. If, however, the solutions containing the intermediate were heated under CO (1 atm), Ru(dppe)(CO)$_3$ was quantitatively regenerated (Figure 2c), and the corresponding aromatic amine was observed. Phosphorus NMR spectroscopy confirmed the rapid consumption of Ru(dppe)(CO)$_3$ upon reaction with *p*-chloronitrobenzene. Three major intermediates appeared successively[9] before reformation of Ru(dppe)(CO)$_3$ became significant (1 day at 25 °C). It is noteworthy that all intermediates exhibited a two-band pattern indicating nonequivalent phosphorus atoms of the dppe ligand.

EPR spectroscopy confirmed the formation of radicals with the observation of a multiplet (a_N = 11.4 G; $a_{H(ortho)}$ = 3.2 G) centered at g = 2.013 after reacting Ru(dppe)(CO)$_3$ with *p*-chloronitrobenzene. The signal intensity indicated that the concentration of the radical was small compared to the initial concentration of the nitroaromatic. *The identical pattern was observed regardless whether the starting substrate was a nitro- or nitrosoarene and results from the radical anion of p-nitrosochlorobenzene.*[10]

The following reactions can account for the observations. In eq 2 and 3, a single-electron-transfer step is proposed based on

$$\mathrm{Ru(dppe)(CO)_3 + ArNO_2 \rightleftharpoons ArNO_2{}^{\bullet -} + [Ru(dppe)(CO)_3]^{\bullet +}} \quad (2)$$

$$\mathrm{ArNO_2{}^{\bullet -} + [Ru(dppe)(CO)_3]^{\bullet +} \rightarrow CO_2 + Ru(dppe)(CO)_2(\eta^2\text{-}ArNO)} \quad (3)$$

(1) the precedent found in the work by Berman and Kochi[8] and (2) the similarity in oxidation potential of nitro- and nitrosoarenes.[11] If the nitrosoarene coordinates to the Ru^{2+} as an [η^2-ArNO]$^{2-}$ ligand, the oxygen could undergo a migratory insertion onto a CO ligand (eq 4). Subsequent CO addition (eq 5) would stabilize the first observable intermediate having structure

$$\mathrm{Ru(dppe)(CO)_2(\eta^2\text{-}ArNO) \rightleftharpoons Ru(dppe)(CO)[N(Ar)OC(O)]} \quad (4)$$

$$\mathrm{Ru(dppe)(CO)[N(Ar)OC(O)] + CO \rightarrow Ru(dppe)(CO)_2[N(Ar)OC(O)]\ (I)} \quad (5)$$

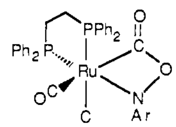
I.[12] The equilibria in 6 and 7 allow for the generation of I from ArNO and Ru(dppe)(CO)$_3$. They also suggest that [Ru(dppe)(CO)$_3$]$^{\bullet +}$ (or an intermediate in eq 6 such as Ru(dppe)(CO)$_3$(η^1-ArNO) would be favored under catalytic conditions (high CO pressure and excess substrate). The nitrene complex proposed as a product of eq 8 could be readily protonated by

$$\mathrm{Ru(dppe)(CO)_2(\eta^2\text{-}ArNO) + CO \rightleftharpoons [Ru(dppe)(CO)_3]^{\bullet +} + ArNO^{\bullet -}} \quad (6)$$

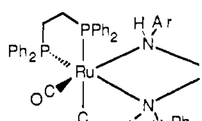
$$\mathrm{ArNO^{\bullet -} + [Ru(dppe)(CO)_3]^{\bullet +} \rightleftharpoons Ru(dppe)(CO)_3 + ArNO} \quad (7)$$

$$\mathrm{Ru(dppe)(CO)_2[N(Ar)OC(O)] \rightarrow CO_2 + Ru(dppe)(CO)_2(NPh)} \quad (8)$$

methanol. A possible dimeric structure of this species, II, would explain both its stability and the two-band IR pattern in the cationic, ν_{CO} region.



I



II

On a longer time scale, methoxide could react with the d^6 Ru^{2+} amido complex leading, via β-hydrogen elimination of formaldehyde (which has been trapped as ArN=CH$_2$ in catalytic reactions), to a hydridoamido complex, which could reductively eliminate aniline. As the pressure of CO increases, CO addition

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[7] Baker, P. K.; Connelly, N. G.; Jones, B. M. R.; Maher, J. P.; Somer, K. R. *J. Chem. Soc., Dalton Trans.* **1980**, 579.

[8] Berman, R. S.; Kochi, J. K. *Inorg. Chem.* **1980**, *19*, 248–254.

[9] ^{31}P NMR data [benzene/MeOH (5/1), ppm relative to external H$_3$PO$_4$]: first intermediate; 47.2, 51.7. Second intermediate; 65.8, 67.7. Third intermediate; 43.7, 44.4.

(10) Russell, G. A.; Geels, E. J.; Smentowski, F. J.; Chang, K.-Y.; Reynolds, J.; Kaupp, G. *J. Am. Chem. Soc.* **1967**, *89*, 3821–3828. The ESR signals for these radical anions were found to be very dependent upon the solvent. The structure of the radical responsible for the observed spectrum under conditions most similar to those described here was assigned to ArN$^{\bullet +}$(O$^-$)ONHAr. This was proposed to form by proton addition to the nitrosoarene adduct of the nitrosoarene radical anion.

(11) Lund, H. In *Organic Electrochemistry*, 2nd ed.; Baizer, M. M., Lund, H., Eds.; Marcel Decker: New York, 1983; Chapter 8.

(12) The IR spectrum of this intermediate is very similar to other neutral Ru(phosphine)$_2$(CO)$_2$X$_2$ complexes, see: Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: Amsterdam, 1984; p 626. The likely existence of isomers of these six coordinate species could be responsible for the breadth of the IR absorptions and could contribute to the complexity of the ^{31}P NMR spectrum.

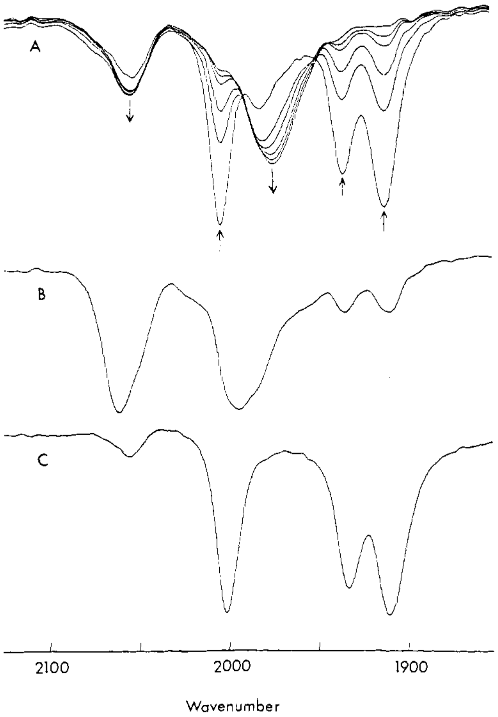

Figure 2. IR spectral changes observed in the stoichiometric reaction of Ru(dppe)(CO)$_3$ with *p*-chloronitrobenzene in *o*-xylene/MeOH: (a) spectral changes during the first 60 m of reaction where the arrows indicate the growth or disappearance of specific absorptions, (b) spectrum after 3 h, and (c) spectrum after heating the solution for 1 h at 95 °C.

could force the migratory insertion of CO into the M–NHAr bond giving a carbamoyl complex that could react with methoxide to form carbamate. Such a competition between CO and MeO$^-$ could be the branch point controlling the observed selectivity of the catalytic reaction.

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Hydroformylation of the C≡C Bond of $(C_5H_5)(PMe_3)_2Ru—C≡C—CH_3$ by $HRe(CO)_5$ To Give an η^1-Aldehyde Complex of Rhenium

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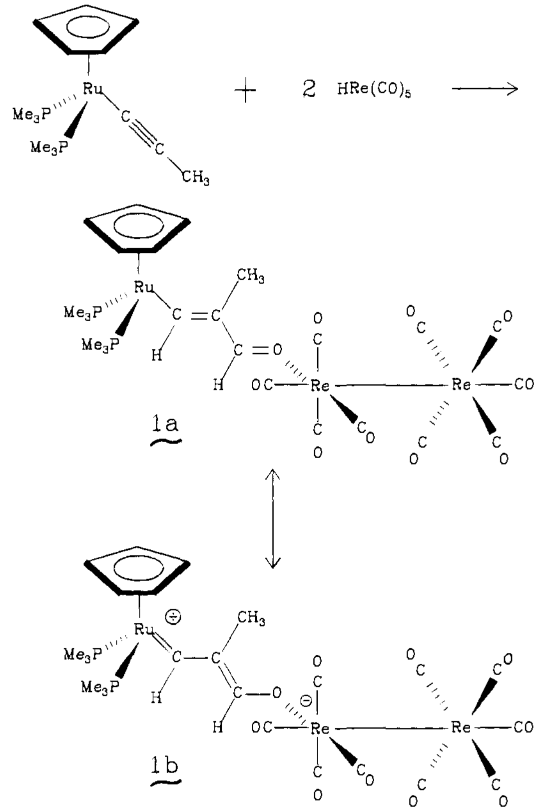
The chemistry of aldehydes bonded to transition metals is not well-developed but has been attracting increasing attention.[1] Most of the previously reported aldehyde complexes exhibit $\eta^2(\pi)$-bonding. We report an unprecedented hydroformylation of the C≡C bond of a metal alkynyl complex by a metal carbonyl hydride, which results in an α,β-unsaturated aldehyde $\eta^1(\sigma)$-bonded to $Re_2(CO)_9$.



(1)

Reaction of $(C_5H_5)(PMe_3)_2Ru—C≡C—CH_3$[2] with excess $HRe(CO)_5$ in CH_3CN (room temperature, 10 min), followed by concentration of the solution, results in precipitation of a bright yellow, air-stable solid in 60% yield. NMR and IR spectra[3] suggested **1a**. The X-ray crystal structure[4] of **1** (Figure 1) confirmed this assignment but also indicated significant contribution from the zwitterionic resonance structure **1b**. In accordance with partial double bond character, the Ru–C distance of **1** (1.986 (9) Å) is shorter than a normal Ru–C single bond[5] but longer than the Ru=C bond in $(C_5H_5)(PMe_3)_2Ru{=}C{=}C(CH_3)H^+$ (1.845 (7) Å).[2] The C=O bond length of 1.263 (12) Å is longer than that observed for acrolein[6] (1.208 (3) Å) and may be compared with the 1.228 (31) Å η^1-aldehyde bond of $(PMe_3)(CO)_3(NO)W(O{=}CHCH{=}CH_2)^+$.[7] Lewis acid adducts of aromatic aldehydes also exhibit η^1-bonding. The C=O bond length deter-

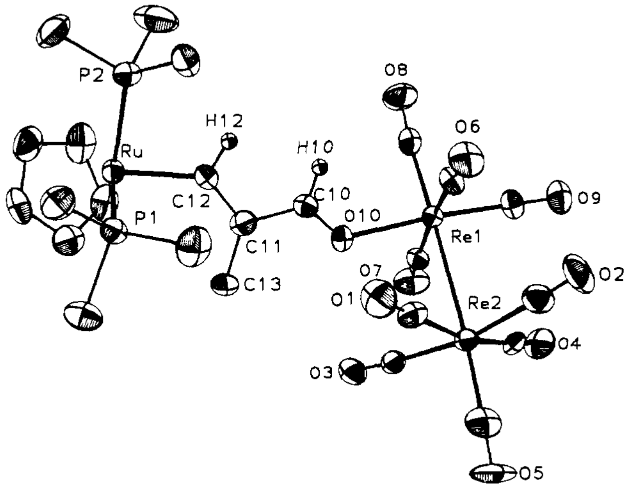


Figure 1. ORTEP drawing of **1** with thermal ellipsoids at the 50% probability level (methyl hydrogens and cyclopentadienyl hydrogens omitted). Selected bond distances (Å) are as follows: Ru–C(12) 1.986 (9); C(12)–C(11) 1.389 (13); C(11)–C(10) 1.436 (12); C(10)–O(10) 1.263 (12), O(10)–Re(1) 2.167 (6); Re(1)–Re(2) 3.019 (1).

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(1) For a recent review, see: Huang, Y.-H.; Gladysz, J. A. *J. Chem. Educ.* **1988**, *65*, 298–303.

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