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**Registry No.** **1a**, 16971-33-8; **1c**, 16971-32-7; **1d**, 100678-61-3; **2** (R = $CMe_3$), 100514-77-0; **2** (R = $CH_2Cl$), 100514-78-1; **2** (R = $CF_2Cl$), 100514-80-5; **2** (R = $C_6H_{11}$), 100514-76-9; **3a**, 100678-64-6; **4a** (X = Br), 100678-68-0; **4a** (X = Cl), 100514-81-6; **5**, 100700-64-9; **6**, 100762-93-4; **7**, 100762-95-6; $RuH(OAc)(CO)(PPh_3)_2$, 50661-73-9; $RuCl(OCOCH_2Cl)(CO)(PPh_3)_2$, 84079-95-8; $RuBr(OCOMe)(CO)(PPh_3)_2$, 100837-28-3; $RuH_2(CO)(PPh_3)_3$, 25360-32-1; $OsHCl(CO)(PPh_3)_3$, 16971-31-6.

**Supplementary Material Available:** Tables IX-XI, $F_o/F_c$ values for $OsBr(OCOMe)(CO)(PPh_3)_2$, $RuCl(OCOMe)(CO)(PPh_3)_2$, and $[PPh_3Me]^+[RuCl_2(\mu\text{-}Cl)_3(CO)_2(PPh_3)_2]^-\cdot CH_2Cl_2$, Tables XII-XIV, anisotropic thermal parameters, and Table XV, phenyl C-C ring distances for **4a**, **3a**, and **6** (80 pages). Ordering information is given on any current masthead page.

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# Chemistry and Catalytic Properties of Ruthenium and Osmium Complexes. 3. Development of Highly Active Systems for the Homogeneous Hydrogenation of Aldehydes and Ketones

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The catalytic hydrogenation of aldehydes and ketones to yield the corresponding alcohols exclusively is efficiently achieved by use of a series of 19 ruthenium and 4 osmium complexes containing hydride, phosphine, and carboxylate ligands, under moderate reaction conditions. For complexes $MHX(CO)(PR_3)_3$ the catalytic activity is dependent on X (halide) and independent of R. Evidence is presented for a mechanism involving $MHX(CO)(PR_3)_2$ as the active species and alkoxy-metal intermediates in the cycle. Carboxylate species $MX(OCOR)(CO)(PPh_3)_2$ show a catalytic behavior dependent on the stereochemistry of the complex, on X, and on the electronic nature of the R group. Correlations between $k_{obsd}$ for the catalytic reaction and $pK_a$ of the acid from which carboxylate ligands are derived have been found. This is explained in terms of a mechanism involving a bidentate-monodentate equilibrium for the carboxylate as a key step in the catalysis.

The homogeneous catalytic hydrogenation of aldehydes and ketones is of considerable interest in connection with industrially important reactions such as those involved in the oxo and aldox processes.[1] Furthermore, this reaction may also be of use in synthetic organic chemistry and as a simple model for the widely publicized CO hydrogenation reaction and its implications in Fischer-Tropsch and related chemistry.[2]

Examples of efficient homogeneous catalysts for the hydrogenation of aldehydes and ketones to their corresponding alcohols are still relatively scarce.[3] Prior to our initial reports on the use of hydrido-phosphine complexes of ruthenium,[4] the only compounds of this metal known to reduce aldehydes were $RuH_2(CO)_2(PPh_3)_2$,[5] $RuCl_2(PPh_3)_3$,[6] and $RuCl_2(CO)_2(PPh_3)_2$;[7] for ketone reduction, $RuCl_2(PPh_3)_3$,[8] $RuH_2(PPh_3)_4$,[9] and $H_4Ru_4(CO)_{12}$[10] had been mentioned in the literature. Since then other neutral[11] and anionic[12] hydrido-phosphine ruthenium complexes were reported to catalytically hydrogenate aldehydes and ketones. We have recently published some preliminary results on the use of carboxylate derivatives of ruthenium for aldehyde hydrogen-

**Table I.** Hydrogenation of Propionaldehyde[a]

| catalyst no. | catalyst compd | $10^2 k_{obsd}$, $min^{-1}$ |
|---|---|---|
| 1 | $RuHCl(CO)(PPh_3)_3$ | 3.50 ± 0.32 |
| 2 | $RuHBr(CO)(PPh_3)_3$ | 2.02 ± 0.10 |
| 3 | $RuHCl(CO)(PCy_3)_2$ | 3.85 ± 0.57 |
| 4 | $RuCl(OCOEt)(CO)(PPh_3)_2$ | 2.15 ± 0.22 |
| 5 | $RuCl(OCOMe)(CO)(PPh_3)_2$ | 2.50 ± 0.25 |
| 6 | $RuBr(OCOMe)(CO)(PPh_3)_2$ | 2.39 ± 0.15 |
| 7 | $RuCl(OCOPh)(CO)(PPh_3)_2$ | 3.04 ± 0.30 |
| 8 | $RuCl(OCOCH_2Cl)(CO)(PPh_3)_2$ | 5.03 ± 0.39 |
| 9 | $[Ru_2(\mu\text{-}OCOCF_3)(\mu\text{-}Cl)_2(CO)_2(PPh_3)_4]CF_3CO_2$ | 3.16 ± 0.20 |
| 10 | $[Ru_2(\mu\text{-}H)(\mu\text{-}Cl)_2(CO)_2(PPh_3)_4]BF_4$ | 1.33 ± 0.07 |
| 11 | $RuH(OCOPh)(CO)(PPh_3)_2$ | 2.04 ± 0.19 |
| 12 | $RuH(OCOEt)(CO)(PPh_3)_2$ | 2.22 ± 0.15 |
| 13 | $RuH(OCOCy)(CO)(PPh_3)_2$ | 2.48 ± 0.16 |
| 14 | $RuH(OCOCMe_3)(CO)(PPh_3)_2$ | 2.54 ± 0.21 |
| 15 | $RuH(OCOMe)(CO)(PPh_3)_2$ | 2.54 ± 0.25 |
| 16 | $RuH(OCOCH_2Cl)(CO)(PPh_3)_2$ | 2.62 ± 0.16 |
| 17 | $RuH(OCOCHCl_2)(CO)(PPh_3)_2$ | 5.23 ± 0.59 |
| 18 | $RuH(OCOCF_2Cl)(CO)(PPh_3)_2$ | 6.13 ± 0.42 |
| 19 | $RuH(OCOCF_3)(CO)(PPh_3)_2$ | 6.70 ± 0.46 |
| 20 | $OsHCl(CO)(PPh_3)_3$ | 2.16 ± 0.12 |
| 21 | $OsHBr(CO)(PPh_3)_3$ | 1.75 ± 0.12 |
| 22 | $OsCl(OCOMe)(CO)(PPh_3)_2$ | 3.39 ± 0.26 |
| 23 | $OsBr(OCOMe)(CO)(PPh_3)_2$ | 2.59 ± 0.24 |

[a] In toluene; 150 °C; 30 atm of $H_2$; [substrate] = 1.4 M; [catalyst] = $1.4 \times 10^{-3}$ M; selectivity >98% for *n*-PrOH.

(1) (a) Pruett, R. L. *Adv. Organomet. Chem.* **1979**, *17*, 1-60. (b) Cornils, B.; Mullen, A. *Hydrocarbon Process.* **1980**, *59*, 93-102. (c) Masters, C. "Homogeneous Transition-Metal Catalysis—A Gentle Art"; Chapman Hall: London, 1981; pp 102-135. (d) Cropley, J. B.; Burgess, L. M.; Loke, R. A. *CHEMTECH* **1984**, 374-380.
(2) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61-104. Sneeden, R. P. A. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: London 1982; Vol. 8, Chapter 50.2.
(3) Mestroni, G.; Camus, A.; Zassinovich, G. In "Aspects of Homogeneous Catalysis"; Ugo, R., Ed.; D. Reidel: Dordrecht, The Netherlands, 1981; Vol. 4, pp 71-98.
(4) (a) Sánchez-Delgado, R. A.; de Ochoa, O. L. *J. Mol. Catal.* **1979**, *6*, 303-305. (b) *J. Organomet. Chem.* **1980**, *202*, 427-434. (c) Sánchez-Delgado, R. A.; Andriollo, A.; de Ochoa, O. L.; Suárez, T.; Valencia, N. *Ibid.* **1981**, *209*, 77-83.
(5) Sánchez-Delgado, R. A.; Bradley, J. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 399-404.
(6) Tsuji, J.; Suzuki, H. *Chem. Lett.* **1977**, 1085-1086.
(7) Strohmeier, W.; Steigerwald, H. *J. Organomet. Chem.* **1977**, *129*, C43-C46.
(8) Kruse, W. M. U.S. Patent 4 024 193, 1977.
(9) Cole-Hamilton, D. J.; Wilkinson, G. *Nouv. J. Chim.* **1977**, *1*, 141-155.
(10) Frediani, P.; Matteoli, U.; Bianchi, M.; Piacenti, F.; Menchi, G. *J. Organomet. Chem.* **1978**, *150*, 173-178.
(11) Strohmeier, W.; Wiegelt, L. *J. Organomet. Chem.* **1978**, *145*, 189-194; **1979**, *171*, 121-129.
(12) Grey, R. A.; Pez, G. R.; Wallo, A. *J. Am. Chem. Soc.* **1981**, *103*, 7536-7542.

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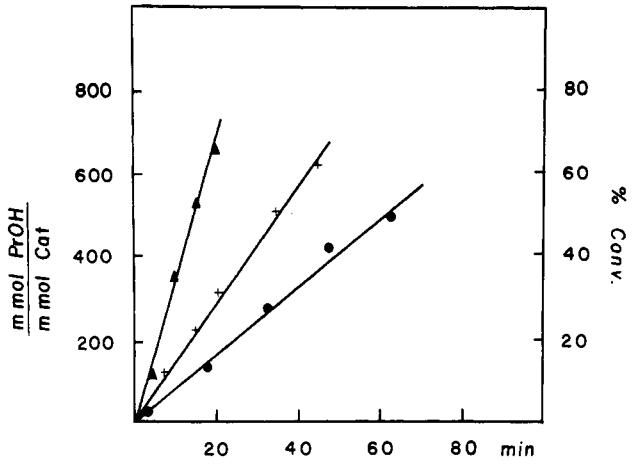



**Figure 1.** Hydrogenation of propionaldehyde with (+) **1**, (▲) **19**, (●) **21**. Conditions are as in Table I. Time values for **21** are corrected for a 10-min induction period (see Experimental Section).

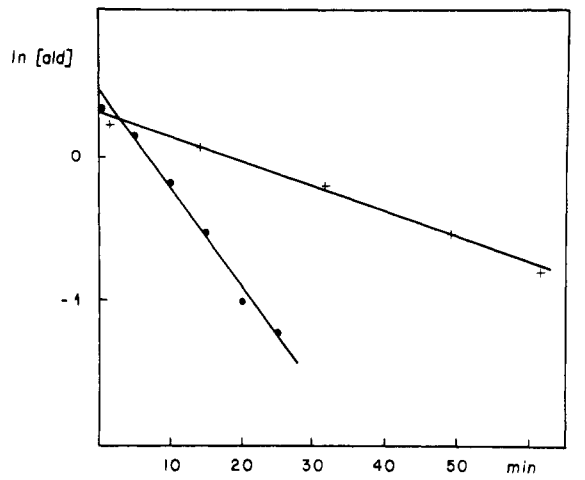



**Figure 2.** Hydrogenation of propionaldehyde with (●) **19** and (+) **21** showing rate dependence on substrate concentration (conditions as in Table I).

ation,[13] and about the same time Jung and Garrou reported the use of bis(trifluoroacetato)ruthenium complexes for the same reaction.[14]

Concerning osmium compounds, there is, to our knowledge, no precedent in the literature for catalytic activity in the homogeneous hydrogenation of the carbonyl group, except for our own recent reports on the use of $OsHBr(CO)(PPh_3)_3$.[15]

In this paper we describe our approach toward a rational design and development of highly efficient catalytic systems derived from ruthenium and osmium complexes for the homogeneous hydrogenation of aldehydes and ketones under moderate reaction conditions; additionally, mecanistic schemes are proposed to account for our results. The synthetic and structural aspects of the transition-metal complexes used in this work are described in the preceding paper of this series.[16]

## Results and Discussion

Table I shows the results of hydrogenating propionaldehyde with 23 different catalysts derived from ruthenium and osmium complexes. The reactions can be carried out at 100 °C and 1 atm of $H_2$, but rates are experimentally more convenient at 150 °C and 30 atm of $H_2$. Toluene was the solvent of choice, since it also serves as an internal test for the homogeneity of the reaction; we do not observe any hydrogenation of the aromatic ring during our catalytic runs, whereas such reduction is extensive in the presence of metallic ruthenium.[17]

Under these conditions the aldehyde is completely, exclusively, and rapidly converted to the corresponding alcohol; all the reactions were carried out under constant $H_2$ pressure and followed by measuring (GLC) the disappearance of the aldehyde and the appearance of the alcohol with time. The production of *n*-propanol increases linearly with time up to at least 50% conversion in all cases; selected examples of reaction behavior are shown in Figure 1. The osmium complexes displayed a ~10 min induction period, after which a linear plot is also obtained, as exemplified for complex **21** in Fig. 1. (For further details see the Experimental Section).

We have previously reported that the rate of hydrogenation of propionaldehyde catalyzed by **1** shows a first-order dependence with respect to aldehyde concentration.[4c] This is also the case for all the other complexes in Table I. Figure 2 shows, as examples of this type of kinetics, runs for the catalysts showing the highest (**19**) and the lowest (**21**) activities. From this kind of plot the observed rate constants ($k_{obsd}$) listed in Table I were obtained (see Experimental Section).

Although the values for $k_{obsd}$ are all rather similar, some significant differences are observed, which indicate the intermediacy of different species, and can be correlated to structural features and interpreted in mechanistic terms.

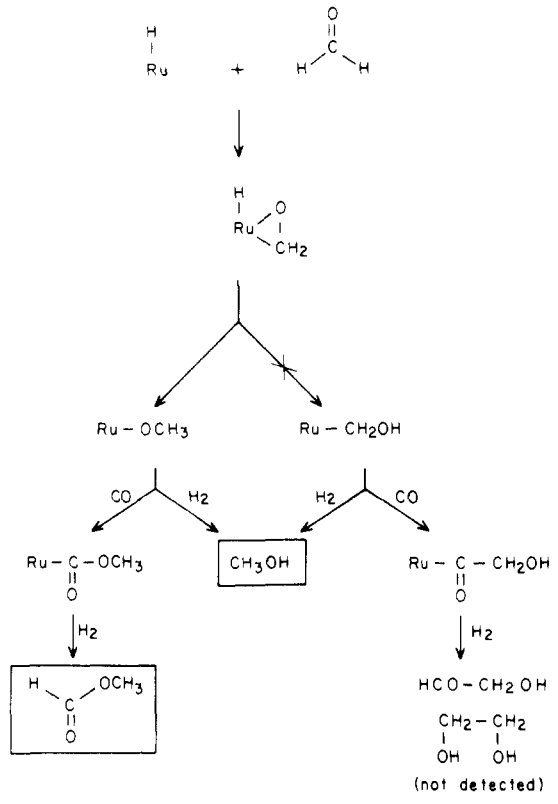
**The Hydrido–Phosphine System $RuHCl(CO)(PPh_3)_3$ and Related Complexes.** As a starting point for any design of a C=O-bond hydrogenation catalyst, and by analogy with other well-known hydrogenation reactions,[1c,18] the basic electronic requirements for a metal complex to be active would be (i) at least one vacant coordination site or labile ligand in order to accommodate the substrate molecule and (ii) a stable pair of oxidation states $x$ and $x + 2$ necessary for oxidative-addition–reductive-elimination equilibria likely to be involved in this type of catalytic cycle.

For ruthenium, the pair of oxidation states II ⇌ IV tends to be more adequate for catalytic reactions than the pair 0 ⇌ II.[18] In our previous work, we tested a variety of known complexes of general stoichiometry $RuX_2L_{3,4}$ and found them to be catalytically active for C=O bond reduction under moderate conditions;[4] in order to avoid undesiderable aldehyde decarbonylation side reactions, which take place for complexes containing exclusively hydride and phosphine ligands[4] (and lead to catalyst poisoning in related rhodium systems),[19] the presence of at least one carbonyl ligand is required. Of this series of complexes the most convenient catalyst precursor, viz. $RuHCl(CO)(PPh_3)_3$ (**1**), was studied in detail. In view of its high activity selectivity and stability,[4] combined with a straightforward synthesis,[20] this is perhaps the most efficient catalyst for the homogeneous hydrogenation of aldehydes and ketones hitherto described.

However, several questions regarding this sytem remained unanswered in our previous report[4] such as the nature of the active species in solution and the mode of hydride transfer to the coordinated C=O bond (i.e migration from the metal to the carbon atom to yield a metal–alkoxy intermediate or to the oxygen atom to produce a metal–hydroxyalkyl species). Perhaps most im-

(13) Sánchez-Delgado, R. A.; Andriollo, A.; Doppert, K.; Ramirez, C.; Valencia, N. *Acta Cient. Venez.* **1982**, *33*, 23–25.
(14) Jung, C. W.; Garrou, P. E. *Organometallics* **1982**, *1*, 658–666.
(15) Sánchez-Delgado, R. A.; Andriollo, A.; Valencia, N. *J. Chem. Soc., Chem. Commun.* **1983**, 444–445; *J. Mol. Catal.* **1984**, *24*, 221–224. Part 1 of this series: Sánchez-Delgado, R. A.; Andriollo, A.; Gonzâlez, E.; Valencia, N.; León, V.; Espidel, J. *J. Chem. Soc., Dalton Trans.* **1985**, 1859–1863.
(16) Sánchez-Delgado, R. A.; Thewalt, U.; Valencia, N.; Andriollo, A.; Márquez, R.-L.; Puga, J.; Schöllhorn, H.; Klein, H.-P.; Fontal, B. *Inorg. Chem.*, preceding paper in this issue.
(17) We have generated Ru metal by decomposing $Ru(acac)_3$ in toluene/propionaldehyde mixtures at 150 °C and 30 atm of $H_2$. After 1 h, both *n*-propanol and methylcyclohexane are detected by gas chromatography.
(18) James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973. "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: London, 1982; Vol. 8, Chapter 51; Bennett, M. A.; Matheson, T. W. *Ibid.* Vol. 4, Chapter 32.9.
(19) Jardine, F. H.; Wilkinson, G. *J. Chem. Soc. C* **1967**, 270–271.
(20) Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 48.

**Scheme I**

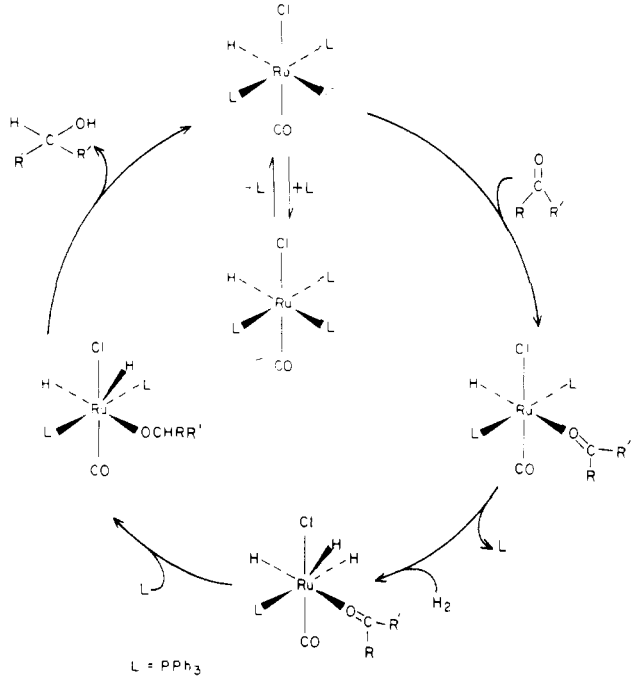



portantly, we wanted to investigate the possibility of enhancing and controlling the catalytic activity by rational modifications of the molecular structure.

We now find that when hydrogenation of, e.g., propionaldehyde is carried out in dilute toluene solution (<2 M) under up to 30 atm of $H_2$ and 150 °C for ca. 2 h with careful exclusion of oxygen, conversions of ~100% are achieved and the catalyst is recovered unchanged in essentially quantitative yields. Furthermore, the catalyst is stable in the pure solvent and unreactive toward hydrogen and/or alcohols in the absence of aldehydes or ketones under reaction conditions and times analogous to those of catalytic runs. We therefore believe the active species to be a complex closely related to the precursor $RuHCl(CO)(PPh_3)_3$; probably the 16-electron species derived from it by phosphine dissociation. The uncharacterized mixtures previously reported to be recovered from the catalytic runs are produced in our system,[4] and probably in another reported case,[14] during hydrogenation of the neat substrate or highly concentrated solutions, or if oxygen is allowed in the reaction medium. Attempts to characterize stable Ru–aldehyde complexes from the reactions of $RuHCl(CO)(PPh_3)_3$ with various aldehydes (RCHO, R = H, Me, Et, Ph) in the absence of $H_2$ have met with no success; $\eta^2$-acyl[21] or carboxylate[22] complexes have been previously reported to form under similar conditions.

Metal–alkoxy or –hydroxyalkyl intermediates could not be isolated either,[23] but we have obtained evidence for a pathway involving the former by the reaction of formaldehyde with *syngas* catalyzed by $RuHCl(CO)(PPh_3)_3$ (Scheme I). This leads to production of methanol and methylformate exclusively, while no glycolaldehyde or its hydrogenation product ethylene glycol, arising from hydrocarbonylation of a hydroxyalkyl intermediate, could be detected. This is in agreement with the direct hydrogenation of carbon monoxide catalyzed by $Ru(CO)_5$,[24] which is thought[24b] to occur via prior formation of a metal–formaldehyde complex, and yields methanol–methylformate mixtures.

**Scheme II**




Earlier unsubstantiated mechanistic proposals involving ruthenium–hydroxyalkyl intermediates in the hydrogenation of aldehydes catalyzed by $RuH_2(CO)_2(PPh_3)_2$[5] are thus probably incorrect.

These findings, together with our earlier kinetic and other data[4] allow us to propose a general schematic mechanism for the $RuHCl(CO)(PPh_3)_3$-catalyzed hydrogenation of C=O bonds, as shown in Scheme II. It has been previously shown that the most labile phosphine ligand in this complex is the one *trans* to the hydride;[25] this suggests that the incoming substrate will occupy that particular coordination site. Formation of the metal–alkoxy intermediate is therefore likely to take place during or after addition of hydrogen to the metal, since transfer of the hydride to a group trans to it is stereochemically unfavored. Reductive elimination of the alcohol regenerates the active 16-electron species $RuHCl(CO)(PPh_3)_2$, which will take up $PPh_3$, or a substrate molecule, to restart the cycle.

As a further development we have studied the possibility of improving the properties of this very active system by a series of appropriate molecular modifications.

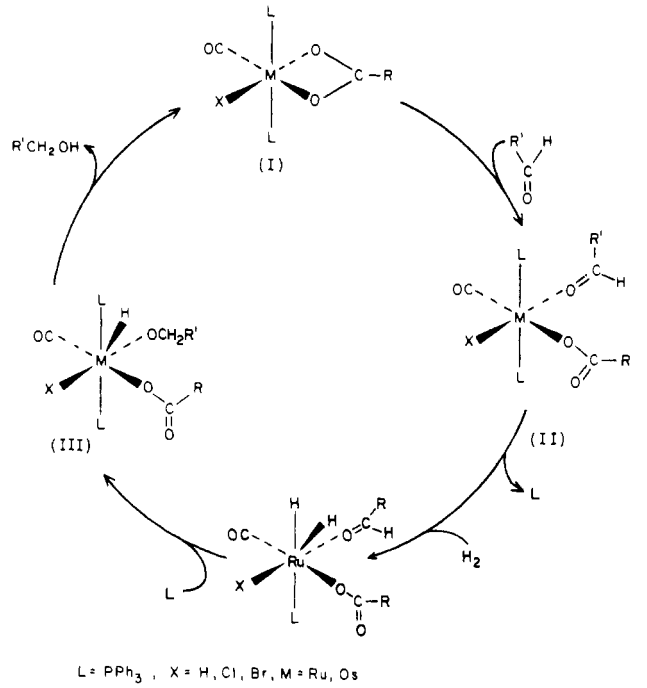
**Variation of Halide and Phosphine Ligands in 1.** As shown in Table I a *decrease* in the rate of aldehyde hydrogenation is observed on going from the chlorinated (**1**) to the brominated (**2**) complex; this is a consistent trend for other ruthenium and osmium complexes (vide infra). The fluoro and iodo analogues are not known and we have not succeeded in their syntheses as yet.

The tricyclohexylphosphine complex (**3**)[26] catalyzed the reaction at essentially the same rate as the triphenylphosphine analogue (**1**).

**Carboxylate Systems and Related Species.** During our studies concerning $RuHCl(CO)(PPh_3)_3$ it was observed that addition of small amounts of acetic acid to the reaction mixture caused an increase in the hydrogenation rate.[4] One possible explanation for

(21) Hitch, R. R.; Sears, C. T. *J. Chem. Soc., Chem. Commun.* **1971**, 777–778.
(22) McGuiggan, M. F.; Pignolet, L. H. *Cryst. Struct. Commun.* **1978**, *7*, 583–588.
(23) (a) We once isolated a compound from a catalytic mixture, whose analytical and spectroscopic data were in agreement with the formulation $RuCl(OPr\text{-}n)(CO)(PPh_3)_3$.[23b] This behavior, however, has not been reproducible and we have not been able to obtain this compound again by this or other methods. (b) Sánchez-Delgado, R. A.; de Ochoa, O. L.; Suárez, T. "Abstracts of Papers"; IX International Conference on Organometallic Chemistry, Dijon, France, 1979; No. P42T.
(24) (a) Bradley, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 7419–7421. (b) Dombeck, B. D. *J. Am. Chem. Soc.* **1980**, *102*, 6855–6857.
(25) Douglas, P. G.; Shaw, B. L. *J. Chem. Soc. A* **1970**, 1556.
(26) Moers, F. G.; Langhout, J. P. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 591. James, B. R.; Preece, M.; Robinson, S. D. *Adv. Chem. Ser.* **1982**, *No. 196*, 145–162.

**Scheme III**




this effect was the formation of carboxylate complexes, according to eq 1, a reaction studied in detail by Robinson and co-workers as a synthetic route to carboxylate derivatives of group 8 metals.[27]

$$RuHCl(CO)(PPh_3)_3 + RCO_2H \rightarrow RuCl(OCOR)(CO)(PPh_3)_2 + H_2 + PPh_3 \quad (1)$$

Furthermore, the coordination properties of carboxylate ligands, combining moderate stability with relatively high lability, render them particularly appropriate for catalytic reactions.[28] There is also a precedent for aldehyde hydrogenation catalysis using iridium hydrides in acetic acid as the solvent,[29] where acetate species are thought to be formed.

This led us to the idea of modifying our catalyst precursor by the introduction of a carboxylate ligand, according to eq 1. A further advantage of this modification is that the great variety of substituents that can be attached to the carboxylic group provides a simple means of controlling the electronic and steric properites of this ligand, thereby controlling to a certain extent the catalytic activity of the system.

Table I shows the results of hydrogenating propionaldehyde with a series of halo-carboxylate-Ru(II) complexes (**4**–**8**), together with $RuHCl(CO)(PPh_3)_3$ for comparison.

As can be seen from these data, carboxylate complexes containing electron-*releasing* substituents (i.e. R = Me, Et, Ph) are in fact slightly *less* active than $RuHCl(CO)(PPh_3)_3$. The increased activity observed on adding small amounts of acetic acid to the hydride precursor[4] are probably best explained in terms of a hydrolytic cleavage of the alkoxy–metal intermediate, similar to that proposed by Schrock and Osborn[30] for the rhodium-catalyzed hydrogenation of ketones in presence of water; in fact, small amounts of water produced an effect on the $RuHCl(CO)(PPh_3)_3$ system similar to that of acetic acid.

The lower activity of these carboxylate complexes may be explained in terms of the mechanism shown in Scheme III. (X = Cl, Br; L = $PPh_3$). We postulate that the coordination site occupied by the aldehyde molecule in species II is made available

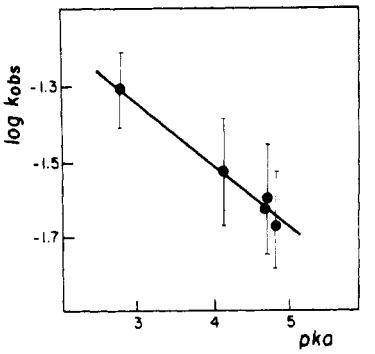
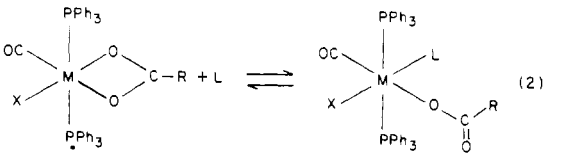



**Figure 3.** Hydrogenation of propionaldehyde with $RuCl(OCOR)(CO)(PPh_3)_2$, showing the relation between catalytic activity and the nature of R (conditions as in Table I).

by opening the carboxylate chelate in I. Although we have not been able to isolate or detect such an intermediate, this type of equilibria (eq 2) is known for related compounds, and stable




products have been characterized for L = CO, $PPh_3$,[31] where the incoming ligand occupies the site trans to the X ligand and the Ru–O bond trans to CO remains intact.

Oxidative addition of $H_2$ followed by hydride transfer to the carbon atom (II → III) yields the 7-coordinate 18-electron Ru(IV)–alkoxy intermediate, which upon reductive elimination of the product alcohol regenerates the active species (I).

It is possible that for electron-releasing R groups the chelate bond is strong enough to maintain the equilibrium largely displaced toward species I, thereby making the overall catalytic rate comparatively low.

One way to overcome this difficulty would be to introduce electron-*withdrawing* R groups, which will tend to favor the monodentate coordination mode and thus produce higher catalytic rates.

One previously unknown compound in the series $RuCl(OCOR)(CO)(PPh_3)_2$, containing a moderately electron-withdrawing carboxylate substituent can be obtained by reaction of $RuHCl(CO)(PPh_3)_3$ with $CH_2ClCO_2H$.[16]

The monochloro acetate complex (**8**), as expected, indeed catalyzes the hydrogenation of propionaldehyde at considerably faster rates than the other complexes in the series (Table I). Moreover, the $pK_a$ values of the acids from which the carboxylate ligands are derived are a good measure of the electron-attracting or -withdrawing properties of the R group attached to the carboxylic carbon atom. Therefore, the extent to which the equilibrium is displaced toward the monodentate form of the complex (II) must be related to these $pK_a$ values on the one hand and to the catalytic rates on the other. A plot of log $k_{obsd}$ vs. $pK_a$ (Figure 3) shows a linear correlation, in excellent agreement with our predictions based on the mechanism in Scheme III.

Replacement of the chloride in **5** by a bromide, as in the new compound **6**, results in a decreased catalytic activity, in accord with our observations on the effect of changing halide ligands in the carboxylate-free systems **1** and **2** (Table I).

Attempts to prepare other unknown isostructural complexes with electron-withdrawing R groups have not been successful, and it appears that $RuHCl(CO)(PPh_3)_3$ tends to react with strong acids to yield dinuclear compounds.[16] This trend is of interest in itself, and we have followed it in some detail. Robinson and co-workers reported[32] that the reaction of $RuHCl(CO)(PPh_3)_3$

(27) Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1973**, 1912–1920.
(28) Dobson, A.; Robinson, S. D. *Platinum Met. Rev.* **1976**, *20*, 36–43.
(29) Coffey, R. S. *J. Chem. Soc., Chem. Commun.* **1967**, 923.
(30) Schrock, R. R.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1970**, 567–568.
(31) Dobson, A.; Robinson, S. D. *Inorg. Chem.* **1977**, *16*, 1321–1328.
(32) Dobson, A.; Robinson, S. D.; Uttley, F. *J. Chem. Soc., Dalton Trans.* **1975**, 370–377.

**Table II.** Hydrogenation of Acetone[a]

| catalyst | turnover no. |
|---|---|
| $RuHCl(CO)(PPh_3)_3$ | 120 |
| $OsHBr(CO)(PPh_3)_3$ | 125 |
| $RuCl(OCOEt)(CO)(PPh_3)_2$ | 120 |
| $RuCl(OCOMe)(CO)(PPh_3)_2$ | 100 |
| $RuCl(OCOPh)(CO)(PPh_3)_2$ | 90 |
| $[Ru_2(\mu\text{-}OCOCF_3)(\mu\text{-}Cl)_2(CO)_2(PPh_3)_4]CF_3CO_2$ | 90 |

[a] In toluene; 150 °C, 30 atm of $H_2$, [substrate]:[catalyst] = 1000; turnover in mol of product/mol of cat (in 4 h); selectivity >95% for *i*-PrOH.

with $CF_3CO_2H$ yields an intractable uncharacterized material. We have reinvestigated this reaction and isolated high yields of a cationic dinuclear compound $[Ru_2(\mu\text{-}Cl)_2(\mu\text{-}OCOCF_3)(CO)_2(PPh_3)_4]^+CF_3CO_2^-$ (**9**).[16] This is also a powerful catalyst for the hydrogenation of aldehydes (Table I), ketones (Table II), olefins,[33a] and nitro compounds.[33b]

Another dinuclear complex $[Ru_2(\mu\text{-}H)(\mu\text{-}Cl)_2(CO)_2(PPh_3)_2]BF_4$ (**10**) has been prepared in high yields by the action of $HBF_4$ on $RuHCl(CO)(PPh_3)_3$.[16] This complex will also effect hydrogenation of aldehydes (Table I) and other catalytic reactions.[33] It appears that the reactions between $RuHCl(CO)(PPh_3)_3$ and strong organic or inorganic acids provide a series of dinuclear complexes structurally very interesting and catalytically highly active but unsuitable for comparison with the mononuclear catalysts in connection with the mechanistic Scheme III. The chemistry of these dinuclear systems will be the subject of a separate report.

A convenient set of isostructural mononuclear carboxylate complexes of Ru(II) is provided by the series $RuH(OCOR)(CO)(PPh_3)_2$ (**11–19**). Some of these complexes have been previously prepared by Robinson and co-workers,[27,32] and we have synthesized new members of the family by slight modifications of the original procedure.[16]

The presence of a hydride rather than a chloride, trans to the carboxylate ligand, results in a single structure for all the complexes, with R groups ranging from $CMe_3$ to $CF_3$ (**11–19**).[16]

The results of propionaldehyde hydrogenation catalyzed by these complexes are also collected in Table I. In this case it is also clearly observed that the catalytic activity is related to the electron-withdrawing character of the carboxylate substituent. A plot of log $k_{obsd}$ *vs.* $pK_a$ of the acid from which the carboxylate ligand is derived shows a smooth correlation for $pK_a < \sim 4$ (**16–19**). For acids with $pK_a > \sim 4$ the activity is essentially independent of the R group (Figure 4). IR and NMR spectra of the complexes after the catalytic runs show the presence of the carboxylate ligand. These findings, together with the known[31] chemistry of ruthenium and osmium–hydrido–trifluoroacetate complexes, indicate that the carboxylate ligand is not fully dissociated during the hydrogenation reaction.

These results are in agreement with our mechanistic postulates in that they show the importance of the monodentate–bidentate equilibrium (eq 2).

**Osmium Systems.** We have extended our studies to osmium compounds, which we have recently found to be considerably active in a variety of homogeneously catalyzed organic reactions.[15] Table I shows the results of propionaldehyde hydrogenation with some osmium complexes (**20–23**).

The activity of these osmium catalysts is in general comparable to that of their ruthenium analogues. A similar trend to that found for ruthenium is observed on going from the chloro to the bromo analogues, i.e. a decrease in catalytic activity. However, the complexes $OsX(OCOMe)(CO)(PPh_3)_2$ (**22, 23**) are considerably more active than $OsHX(CO)(PPh_3)_3$ (**20, 21**), in contrast to the case of $RuX(OCOMe)(CO)(PPh_3)_2$ (**5, 6**) vs. $RuHX(CO)(PPh_3)_3$ (**1, 2**) for which the opposite effect or essentially no effect, respectively, was observed. This can be interpreted in terms of the different stereochemistries found for these compounds by X-ray diffraction and $^{31}P\{^1H\}$ NMR,[16] viz. a trans arrangement of the phosphines for Ru and a cis arrangement for Os.

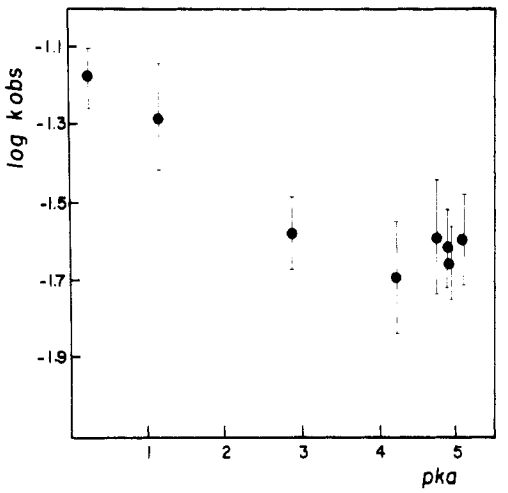
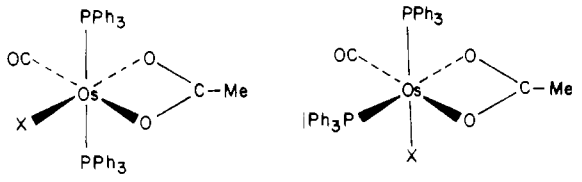



**Figure 4.** Hydrogenation of propionaldehyde with $RuH(OCOR)(CO)(PPh_3)_2$, showing the relation between catalytic activity and the nature of R (conditions as in Table I).




(**5**) X = Cl (**22**) X = Cl

(**6**) X = Br (**23**) X = Br

The presence of the powerful $\sigma$-donor $PPh_3$ trans to the Os–O bond in **22** or **23** should contribute to the opening of the carboxylate chelate; moreover, the bidentate–monodentate transformation would relieve some of the great steric constraint apparent from the solid-state structure of complex **23**.[16]

This, in agreement with our mechanistic considerations, results in an enhanced catalytic activity for the acetate–osmium catalysts with respect to the carboxylate-free systems. In the ruthenium acetate complexes, on the other hand, no particularly serious steric congestion is relieved by opening the carboxylate. Furthermore, the Ru–O bonds are located trans to poorer $\sigma$-donors than $PPh_3$ (CO and Cl), and therefore the bidentate forms, associated with lower rates, are favored.

**Hydrogenation of Ketones.** Hydrogenation of ketones requires more drastic conditions than for aldehydes (Table II). Catalyst lives are shorter, and metal deposition, accompanied by a sharp rise in ketone hydrogenation rate, and appearance of methylcyclohexane, is often observed for the less stable complexes after 2–4-h reaction. In every other respect the considerations described for aldehyde reduction are generally valid for ketones.

Other aliphatic and aromatic aldehydes and ketones are hydrogenated to their corresponding alcohols. $\alpha,\beta$-Unsaturated aldehydes are reduced to the saturated aldehyde, the unsaturated alcohol, or the fully reduced product,[15] depending on the reaction conditions and the catalyst used. The C=C bond of unsaturated ketones is reduced preferentially.

## Experimental Section

Manipulations were carried out under dry nitrogen or argon using Schlenk techniques or a drybox. Solvents and substrates were purified by conventional procedures. The preparation and characterization of the complexes are described in the preceding paper.[16]

GLC analyses were performed on a Varian 3700 chromatograph fitted with a flame ionization detector and a 10-ft 10% SE-30 on Supelcoport stainless-steel column. Quantification was achieved with a Varian

(33) (a) Sánchez-Delgado, R. A.; Valencia, N.; Oramas, A. *Acta Cient. Venez.* **1984**, *35*, 228–231. (b) Sánchez-Delgado, R. A.; Oramas, A., to be submitted for publication.

CDS-401 VISTA data system coupled with the chromatograph, operating with an automatic internal standard method (ethanol was the internal standard).

**Catalytic Runs.** In a typical experiment the catalyst ($7.0 \times 10^{-5}$ mol), the substrate ($7.0 \times 10^{-2}$ mol), the solvent (50 mL), and a stirring bar were placed in a glass-lined stainless-steel autoclave (125 mL, Parr). The autoclave was purged three times with 500 psig of $H_2$ and then charged to the desired pressure. It was then introduced into a thermostated silicone oil bath and magnetically stirred; this was taken as the zero time of the reaction. The pressure was maintained constant throughout the reaction by continuous supply from a high-pressure reservoir. At the end of the run the autoclave was placed in ice, the excess pressure was released and the mixture was inmediately analyzed by GLC.

**Kinetic Measurements and Calculations.** For kinetic measurements, series of autoclaves containing 50-mL aliquots of the solutions containing the catalysts and the substrate were used (conditions as above). The reactions were quenched at different times and immediately analyzed. Mass balance showed that the appearance of the alcohol corresponded to >98% of the disappearance of the aldehyde, indicating that <2% of byproducts were formed.

Plots of alcohol production (in millimoles of alcohol per millimole of Ru per minute) vs. time were linear with very small nonzero intercepts up to at least 50% conversion for all the Ru complexes. For the Os complexes no conversion of the aldehyde was observed for the first ~10 min after which hydrogenation was triggered off and also displayed a linear behavior; in these cases the reaction times used in the plot (see for example Figure 1 for complex **21**) were corrected by substracting 10 min, so that the zero point is taken at the time when hydrogenation actually begins.

At constant catalyst concentration and hydrogen pressure the rate law takes the form $-d[\text{aldehyde}]/dt = k_{obsd}[\text{aldehyde}]$, consistent with linear plots of ln [aldehyde] vs. $t$ (see for instance, Figure 2). The corresponding slopes yielded the values of $k_{obsd}$ listed in Table I. In all calculations conventional linear regression programs were used, and the lines were fitted to $r$ values >0.99. $k_{obsd}$ values were taken as a measure of catalytic activity for comparison purposes.

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**Registry No.** **1**, 61521-25-3; **2**, 100678-61-3; **3**, 100678-62-4; **4**, 100678-63-5; **5**, 100678-64-6; **6**, 100514-70-3; **7**, 68853-49-6; **8**, 100678-65-7; **9**, 100514-72-5; **10**, 100514-74-7; **11**, 100514-75-8; **12**, 50661-74-0; **13**, 100514-76-9; **14**, 100514-77-0; **15**, 50661-73-9; **16**, 100514-78-1; **17**, 100514-79-2; **18**, 100514-80-5; **19**, 60451-51-6; **20**, 100678-66-8; **21**, 100678-67-9; **22**, 100514-81-6; **23**, 100678-68-0; propionaldehyde, 123-38-6; acetone, 67-64-1.

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Contribution from the Department of Chemistry, Faculty of Engineering Science and Faculty of Pharmaceutical Sciences, Osaka University, Toyonaka, Osaka 560, Japan

# Synthesis of Hexanuclear Molybdenum Cluster Alkyl Complexes Coordinated with Trialkylphosphines: Crystal Structures of *trans*-$[(Mo_6Cl_8)Cl_4\{P(n\text{-}C_4H_9)_3\}_2]$ and *all-trans*-$[(Mo_6Cl_8)Cl_2(C_2H_5)_2\{P(n\text{-}C_4H_9)_3\}_2]\cdot 2C_6H_5CH_3$

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Hexanuclear molybdenum cluster chloride complexes coordinated with two trialkylphosphines were prepared, and *trans*-$[(Mo_6Cl_8)Cl_4(PR_3)_2]$ (R = $n$-$C_3H_7$, $n$-$C_4H_9$, $n$-$C_5H_{11}$) and *cis*-$[(Mo_6Cl_8)Cl_4\{P(n\text{-}C_3H_7)_3\}_2]$ were isolated by chromatography. *trans*-$[(Mo_6Cl_8)Cl_4\{P(n\text{-}C_4H_9)_3\}_2]$ (**3**) crystallizes in the monoclinic space group $C2/c$ with $a$ = 29.076 (3) Å, $b$ = 10.301 (1) Å, $c$ = 21.508 (5) Å, $\beta$ = 135.28 (1)°, and $Z$ = 4. The X-ray structure determination confirmed that the two tributylphosphine ligands are coordinated to the trans positions of the octahedral molybdenum cluster core with eight face-bridging and four terminal chlorines. Pertinent distances are Mo–Mo = 2.6162 (8) Å (av), Mo–$Cl^t$ = 2.410 (2) Å (av), Mo–$Cl^b$ = 2.473 (2) Å (av), and Mo–P = 2.619 (2) Å. Derivatives of the types $[(Mo_6Cl_8)Cl_{4-x}R'_x(PR_3)_2]$ ($x$ = 2, 3; R' = $CH_3$, $C_2H_5$, $C_3H_7$, $C_4H_9$, $C_6H_{13}$) were prepared by alkylation of *trans*-$[(Mo_6Cl_8)Cl_4(PR_3)_2]$ with $AlR'_3$. The complex *all-trans*-$[(Mo_6Cl_8)Cl_2(C_2H_5)_2\{P(n\text{-}C_4H_9)_3\}_2]\cdot 2C_6H_5CH_3$ (**6**) crystallizes in the monoclinic space group $P2/c$ with $a$ = 13.855 (2) Å, $b$ = 11.120 (3) Å, $c$ = 20.506 (2) Å, $\beta$ = 95.81 (1)°, and $Z$ = 2. Two ethyl groups, two chlorines, and two tributylphosphines are bonded to the octahedral $Mo_6Cl_8$ core in mutually trans positions. The selected bond distances are Mo–C = 2.21 (3) Å, Mo–P = 2.604 (8) Å, and Mo–$Cl^t$ = 2.421 (8) Å. Detailed structural data are reported. Complex **6** decomposed at around 150 °C, evolving dihydrogen, ethane, ethylene, and small amounts of other gaseous products.

## Introduction

A number of hexanuclear molybdenum cluster halides with the $(Mo_6X_8)^{4+}$ core and anionic and neutral terminal ligands have been prepared,[2] and structures of some of them have been determined.[3] The similarity of the $Mo_6$ cluster core to that of Chevrel phases[4] and the interesting photochemical properties[5] have attracted renewed interest in these molybdenum cluster halide systems. Despite the remarkable stability of the cluster framework the chemistry of the cluster complexes has not been much explored.[6]

The purpose of the present study was to effect the hitherto unreported separation of the cis and trans isomers of the tertiary phosphine complexes $[(Mo_6Cl_8)Cl_4(PR_3)_2]$ and to synthesize cluster alkyl complexes by alkylation of the trans isomers. Although alkyl complexes are considered as intermediates in the cluster catalysis of olefins,[7] very few such complexes have been

(1) (a) Faculty of Engineering Science. (b) Faculty of Pharmaceutical Sciences.

(2) (a) Sheldon, J. C. *J. Chem. Soc.* **1960**, 1007. (b) Sheldon, J. C. *J. Chem. Soc.* **1961**, 750. (c) Cotton, F. A.; Curtis, N. F. *Inorg. Chem.* **1965**, *4*, 241. (d) Cotton, F. A.; Curtis, N. F.; Johnson, B. F. G.; Robinson, W. R. *Inorg. Chem.* **1965**, *4*, 326. (e) Fergusson, J. E.; Robinson, B. H.; Wilkins, C. J. *J. Chem. Soc. A* **1967**, 486. (f) Carmichael, W. M.; Edwards, D. A. *J. Inorg. Nucl. Chem.* **1967**, *29*, 1535. (g) Nannelli, P.; Block, B. P. *Inorg. Chem.* **1968**, *7*, 2423. (h) Field, R. A.; Kepert, D. L.; Taylor, D. *Inorg. Chim. Acta* **1970**, *4*, 113. (i) Hamer, A. D.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 1014.

(3) (a) Guggenberger, L. J.; Sleight, A. W. *Inorg. Chem.* **1969**, *8*, 2041. (b) Schnering, H. G. *Z. Anorg. Allg. Chem.* **1971**, *385*, 75. (c) Healy, P. C.; Kepert, D. L.; Taylor, D.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1973**, 646. (d) Schäffer, H.; Brendel, C.; Henkel, G.; Krebs, B. *Z. Anorg. Allg. Chem.* **1982**, *491*, 275. (e) Okuyama, H.; Taga, T.; Osaki, K.; Tsujikawa, I. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 307.

(4) (a) Michel, J. B.; McCarley, R. E. *Inorg. Chem.* **1982**, *21*, 1864. (b) Hughbanks, T.; Hoffmann, R. *J. Am. Chem. Soc.* **1983**, *105*, 1150.

(5) Maverick, A. W.; Najdzionek, J. S.; MacKenzie, D.; Nocera, D. G.; Gray, H. B. *J. Am. Chem. Soc.* **1983**, *105*, 1878.

(6) (a) Kepert, D. L. "The Early Transition Metals"; Academic Press: London and New York, 1972. (b) Walton, R. A. *Prog. Inorg. Chem.* **1972**, *16*, 1.

(7) (a) Deeming, A. J.; Hasso, S. J. *J. Organomet. Chem.* **1976**, *114*, 313. (b) Shapley, J. R.; Keister, J. B. *J. Am. Chem. Soc.* **1976**, *98*, 1056. (c) Doi, Y.; Koshizuka, K.; Keii, T. *Inorg. Chem.* **1982**, *21*, 2736.

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