steadier concentration of the barium chelate in the gas phase and improved the quality of the thin-film superconductors made in this way.[23]

## Conclusions

The metal β-diketonate complexes used as precursors for MOCVD of thin-film superconductors have been characterized chemically and physically. The alkaline-earth-metal chelates, which are less volatile than the analogous copper(II) and yttrium(III) complexes, are oligomeric. Oligomeric ions were observed by negative chemical ionization mass spectrometry, and the abundances of oligomeric ions in the electron ionization spectra are not dependent upon source pressure. Mass spectral, elemental analysis, and preliminary X-ray results show that the compound previously formulated as $Ba(thd)_2$ is more accurately described by the formula $Ba_5(thd)_9(H_2O)_3(OH)$. The gas-phase chromatographic elution of these complexes is difficult, particularly when a flame ionization detector is used, because the complexes tend to become adsorbed onto the column and may thermally decompose in the chromatographic system. However, gas-phase chromatographic elution of these chelates can be performed more readily at subambient pressure with a mass spectrometer as a detector, and a mixed-metal complex containing both Ba(II) and Ca(II) was eluted when $[Ba(fod)_2]_n$ and $[Ca(fod)_2]_n$ were coinjected. The existence of this species, which can be separated chromatographically, is further evidence that oligomeric species exist within the chromatographic column prior to entrance into the mass spectrometer source. In addition, it has been determined that the addition of excess free ligand improves the chromatographic peak shapes of these alkaline-earth-metal chelates, presumably by breaking down the higher oligomers. This confirms earlier work which showed that the addition of excess protonated ligand to the barium source in MOCVD produces higher quality superconducting thin films that are obtained without the additional β-diketone.[23]

**Acknowledgment.** We thank R. Curtis Haltiwanger for performing the X-ray diffraction analysis to be reported separately. This research was supported, in part, by the National Science Foundation under Grant MSM-8718569 and the Department of Energy under SBIR Grant DOE-ACO5-88ER80642 to Sievers Research, Inc.

Contribution from the Chemistry Center,
Instituto Venezolano de Investigaciones Científicas, Caracas 1020-A, Venezuela

# Chemistry and Catalytic Properties of Ruthenium and Osmium Complexes. 6. Synthesis and Reactivity of $[RuH(CO)(NCMe)_2(PPh_3)_2][BF_4]$, Including the Catalytic Hydroformylation of Hex-1-ene

Roberto A. Sânchez-Delgado,* Merlin Rosales,[†] and Antida Andriollo

*Received August 9, 1990*

The interaction of $RuHCl(CO)(PPh_3)_3$ (**1**) with $CD_3CN$ leads to the formation of a mixture containing two isomeric forms of the complex $RuHCl(CO)(NCCD_3)(PPh_3)_2$ (**2′** + **4′**) plus the cationic species $[RuH(CO)(NCCD_3)_2(PPh_3)_2]^+$ (**3′**), as shown by in situ $^{1}$H and $^{31}$P NMR experiments and other reactivity studies. If **1** is reacted with $CH_3CN$ int he presence of $NaBF_4$, $[RuH(CO)(NCCH_3)_2(PPh_3)_2][BF_4]$ (**3**) is isolated pure in high yields. This cation reacts readily at room temperature with neutral ligands ($PPh_3$, $P(OPh)_3$, $Ph_2PCH_2CH_2PPh_2$, py, CO) by substitution of the acetonitrile trans to the hydride; at 60 °C, both acetonitriles can be displaced. Complex **3** also reacts with anions such as halides and $OAc^-$ to yield the corresponding neutral species or with $Co(CO)_4^-$ to produce the heterobimetallic complex $[Ru(CO)_3(PPh_3)(\mu\text{-}PPh_2)Co(CO)_3]$. All the new complexes were characterized by analytical and spectroscopic (IR, $^{1}$H and $^{31}$P NMR) methods. Complex **3** was also found to catalyze the hydroformylation of hex-1-ene at 120–150 °C and 100 bar $CO/H_2$.

The complex $RuHCl(CO)(PPh_3)_3$ (**1**), first reported by Vaska and Diluzio in 1961,[1] has attracted continuous attention. This cream-colored, air-stable material is rather insoluble in most common solvents, and therefore its characterization has been based on elemental analysis and IR and Raman spectroscopy.[1-3] The stereochemistry of **1** has been assumed to be analogous to those of the related complexes $RuHCl(CO)(PMePh_2)_3$ and $OsHBr(CO)(PPh_3)_3$, which have been characterized by $^{1}$H NMR spectroscopy and X-ray diffraction, respectively.[4,5]

Substitution of a phosphine by other neutral ligands leads to complexes $RuHCl(CO)(PPh_3)_2L$ (L = CO, RNC, $PR_3$, $P(OR)_3$, $P(OR)R'_2$, $P(OR)_2R'$, pySH);[6] in most cases, the incoming ligand occupies the position trans to the hydride. Substitution reactions involving chloride abstraction yield cationic or neutral complexes of the type $[RuH(CO)(PPh_3)_{3-n}L_{1+n}]^{x+}$ ($x = 1$, L = $P(OR)_3$, $n = 1$; $x = 1$, L = $PPh_2(OR)$, $n = 3$; $x = 0$, L = $S_2CY^-$, Y = $NR_2$, OR, $n = 1, 2$).[6a,7] Interaction of **1** with carboxylic acids produces carboxylate species $RuCl(CO)(OCOR)(PPh_3)_2$[3,8] and in the case of trifluoroacetic acid the dimer $\{(\mu\text{-}CF_3CO_2)[Ru(\mu\text{-}Cl)(CO)(PPh_3)_2]_2\}^+\{CF_3CO_2\}^-$.[3] Other related complexes such as $\{(\mu\text{-}H)[Ru(\mu\text{-}Cl)(CO)(PPh_3)_2]_2\}^+$,[3] $\{(\mu\text{-}Cl)[Ru(\mu\text{-}Cl)(CO)(PPh_3)_2]_2\}^-$,[3] and $RuCl(CO)(PPh_3)(\mu\text{-}Cl)_3Ru(CO)(PPh_3)_2$[9] are obtained from the reactions of **1** with $HBF_4$, $CH_2ClCO_2H$, and gaseous HCl, respectively. Similarly, β-diketones react with **1** to produce complexes $RuCl(CO)(\beta\text{-dike})(PPh_3)_2$.[10] Insertion reactions into the Ru–H bond of **1** have been reported for arenediazonium salts,[9] 2-vinylpyridine, methylsorbate, dimethylfumarate, acrylonitrile,[11] carbon disulfide, dialkyl and diarylcarbodiimides, 1,3-diaryltriazenes,[12] and acetylenes.[13]

---

[†] Present address: Departamento de Química, Universidad del Zulia, Maracaibo, Venezuela.

(1) Vaska, L.; Diluzio, J. W. *J. Am. Chem. Soc.* **1961**, *83*, 1262.
(2) Ahmad, N.; Levinson, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 48.
(3) Sânchez-Delgado, R. A.; Thewalt, U.; Valencia, N.; Andriollo, A.; Mârquez-Silva, R. L.; Puga, J.; Schöllhorn, H.; Klein, H.-P.; Fontal, B. *Inorg. Chem.* **1986**, *25*, 1097.
(4) Jenkins, J. M.; Lupin, M. S.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 1787.
(5) Orioli, P.; Vaska, L. *Proc. Chem. Soc. (London)* **1962**, 333.
(6) (a) Creswell, C. J.; Robinson, S. D.; Sahajpal, A. *Polyhedron* **1983**, *6*, 517. (b) Preece, M.; Robinson, S. D.; Wingfield, J. N. *J. Chem. Soc., Dalton Trans.* **1976**, 613.
(7) Sanders, J. R. *J. Chem. Soc. A* **1975**, 2991.
(8) Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans* **1973**, 1912.
(9) McCleverty, J. A.; Seddon, D.; Whiteley, R. N. *J. Chem. Soc., Dalton Trans.* **1975**, 839.
(10) Natarajan, K.; Agarwala, U. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 7. Queirôs, M. A.; Robinson, S. D. *Inorg. Chem.* **1978**, *17*, 310.
(11) Hiraki, K.; Sasada, Y.; Kitamura, T. *Chem. Lett.* **1980**, 449.
(12) Robinson, S. D.; Sahajpal, A. *Inorg. Chem.* **1977**, *16*, 2718, 2722. Brown, L. D.; Robinson, S. D.; Sahajpal, A.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 2728. Harris, A. D.; Robinson, S. D.; Uttley, M. F. *J. Organomet. Chem.* **1979**, *174*, C11. Laing, K. R.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc. Dalton Trans.* **1974**, 1205.

0020-1669/91/1330-1170$02.50/0 © 1991 American Chemical Society

**Table I.** NMR Spectra of New Complexes[a]

| complex | $^1H$ | | | $^{31}P\{^1H\}$ | |
|---|---|---|---|---|---|
| | $\delta_{M-H}$ | $J_{H-P}$ | $\delta_{Me}$ | $\delta$ | $J_{P-P}$ |
| $RuHCl(CO)(PPh_3)_3$ (**1**) | −6.8 (dt) | 105, 24 | | 37.8 (d), 10.3 (t) | 17 |
| $RuHCl(CO)(NCMe)(PPh_3)_2$ (**2**) | −14.3 (t) | 15 | 1.4 | 42.8 (s) | |
| $[RuH(CO)(NCMe)_2(PPh_3)_2]^+$ (**3**) | −13.0 (t) | 17 | 1.4, 1.8 | 44.4 (s) | |
| $RuHCl(CO)(NCMe)(PPh_3)_2$ (**4**) | −12.1 (t) | 15 | 1.6 | 40.8 (s) | |
| $[RuH(CO)(NCMe)(PPh_3)_3]^+$ (**5**) | −8.0 (dt) | 91, 25 | 1.6 | 40.1 (d), 19.9 (t) | 22 |
| $[RuH(CO)(NCMe)(PPh_3)_2(P(OMe)_3)]^+$ (**6**) | −6.5 (dt) | 160, 20 | 1.3 | 44.5 (d), 127.8 (t) | 24 |
| $[RuH(CO)(NCMe)(PPh_3)_2(diphos)]^+$ (**7**) | −8.1 (dt) | 90, 23 | 1.6 | 42.3 (d), 16.5 (m)<br>−14.9 (s) (uncoord) | 17 |
| $[RuH(CO)(NCMe)(py)(PPh_3)_2]^+$ (**8**) | −12.4 (t) | 16 | 1.6 | 46.5 (s) | |
| $[RuH(CO)(py)_2(PPh_3)_2]^+$ (**9**) | −13.1 (t) | 17 | | 45.1 (s) | |
| $[RuH(CO)_2(NCMe)(PPh_3)_2]^+$ (**10**) | −5.3 (t) | 17 | 1.5 | 40.5 (s) | |
| $[RuH(CO)_3(PPh_3)_2]^+$ (**11**) | −6.5 (t) | 16 | | | |
| $RuHI(CO)(NCMe)(PPh_3)_2$ (**12**) | −11.6 (t) | | 1.5 | 43.1 (s) | |

[a] In $CDCl_3$; $\delta$ in ppm from TMS or $H_3PO_4$; $J$ in Hz.

**Table II.** Hydroformylation of Hex-1-ene Catalyzed by **3**[a]

| $T$, °C | $CO/H_2$[b] | additive | % conversion | % hydrocarbons[c] | % aldehydes | % alcohols | $n/i$ |
|---|---|---|---|---|---|---|---|
| 120 | 1 | | 54 | 33 | 14 | 7 | 1.4 |
| 120 | 2 | | 56 | 29 | 21 | 6 | 1.6 |
| 150 | 2 | | 100 | 30 | 10 | 60 | 0.9 |
| 120 | 1 | $P(OPh)_3$ | 69 | 42 | 3 | 24 | 1.4 |
| 150 | 2 | $P(OPh)_3$ | 92 | 56 | 3 | 33 | 1.4 |
| 150 | 2 | $PPh_3$ | 98 | 51 | 5 | 43 | 1.3 |
| 150 | 2 | $PCy_3$ | 97 | 56 | 17 | 24 | 1.0 |

[a] In toluene; 20 h; [substrate]:[cat.] = 100; [additive]:[cat.] = 5. [b] 100 bar. [c] Hexane + hex-2-enes.

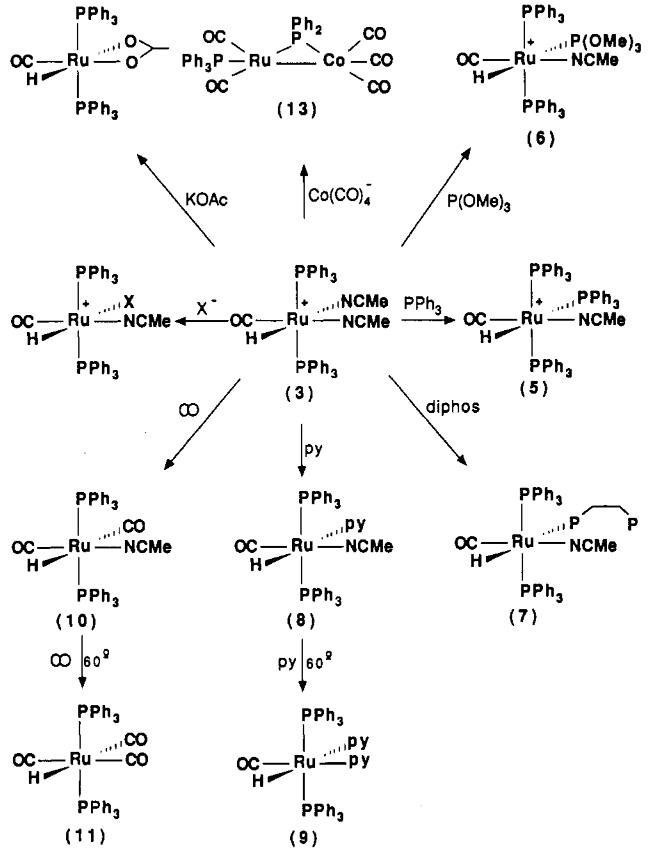
Interest in complex **1** and related species is further enhanced by their catalytic activity in a number or important reactions such as C=C bond migration[14] and hydrogenation of olefins,[15] aldehydes, ketones, $\alpha,\beta$-unsaturated aldehydes,[16] nitroarenes,[17] and N- and S-heterocycles.[18]

Since **1** is an 18-electron species, phosphine dissociation has been generally found (or assumed) to be the first step that generates the active species in catalytic cycles. In our search for more soluble and highly reactive derivatives of **1** we have turned our attention toward the synthesis of cationic complexes containing simple nitrogen-base ligands, which are often more labile than phosphines and may thus result in an enhanced reactivity. Surprisingly, this type of chemistry has been little developed; Roper and co-workers briefly described the synthesis and some reactions of $[RuH(CO)(MeCN)_2(PPh_3)_2][ClO_4]$.[19] While our work was in progress, the reactions of **1** with pyridines[20a] and pyrazoles[20b] were described.

## Results

In this paper we report a $^1H$ and $^{31}P$ NMR study of the interaction of **1** with acetonitrile, leading to the formation of two isomers of $[RuHCl(CO)(MeCN)(PPh_3)_2]$ (**2** + **4**) and the cationic complex $[RuH(CO)(PPh_3)_2(MeCN)_2][BF_4]$ (**3**). We also describe the high-yield synthesis of **3** and its reactivity toward neutral and anionic ligands, leading to a variety of new compounds, as summarized in Scheme I and Table I. This cationic complex has also been found to be a catalyst precursor for the catalytic hydroformylation of hex-1-ene, as shown in Table II.

**Scheme I**



## Discussion

**NMR Study of the Interaction of 1 with MeCN.** Complex **1** dissolves sparingly and slowly in $CD_2Cl_2$; the $^1H$ NMR spectrum of such dilute solutions (Table I) shows a high-field doublet of triplets assigned to a metal–hydride coupled to one trans and two

---

(13) Torres, M. R.; Santos, A.; Ros, J.; Solans, J. *Organometallics* **1987**, *6*, 1091.

(14) Bingham, D.; Webster, D. E.; Wells, P. B. *J. Chem. Soc., Dalton Trans.* **1974**, 1519.

(15) Sânchez-Delgado, R. A.; Valencia, N.; Oramas, B. A. *Acta Cient. Venez.* **1984**, *35*, 228.

(16) Sânchez-Delgado, R. A.; de Ochoa, O. L. *J. Mol. Catal.* **1979**, *6*, 303. Sânchez-Delgado, R. A.; de Ochoa, O. L. *J. Organomet. Chem.* **1980**, *202*, 427. Sânchez-Delgado, R. A., Andriollo, A.; de Ochoa, O. L.; Suârez, T.; Valencia, N. *J. Organomet. Chem.* **1981**, *209*, 77. Sânchez-Delgado, R. A.; Andriollo, A.; Valencia, N. *J. Mol. Catal.* **1984**, *24*, 217. Sânchez-Delgado, R. A., Valencia, N.; Mârquez-Silva, R. L.; Andriollo, A.; Medina, M. *Inorg. Chem.* **1986**, *25*, 1106.

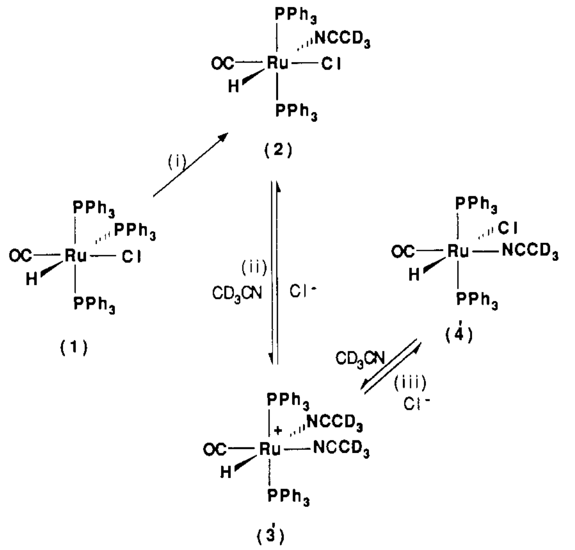
(17) Sânchez-Delgado, R. A.; Oramas, B. A. *J. Mol. Catal.* **1986**, *36*, 283.

(18) Sânchez-Delgado, R. A.; Gonzâlez, E. *Polyhedron* **1989**, *8*, 1431.

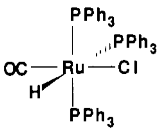
(19) Cavit, B. E.; Grundy, K. R.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* **1972**, 60.

(20) (a) Romero, A.; Vegas, A.; Santos, A.; Martinez-Ripoll, M. *J. Organomet. Chem.* **1987**, *319*, 103. (b) Romero, A.; Vegas, A.; Cuadro, A. *J. Chem. Soc., Dalton Trans.* **1987**, 183.

**Scheme II**



cis phosphine ligands. Correspondingly, the $^{31}P\{^1H\}$ NMR spectrum (Table I) consists of a clear $AX_2$ pattern. These data are consistent with the stereochemistry depicted by **1**, which is analogous to those of well-characterized complexes.[4,5]



(**1**)

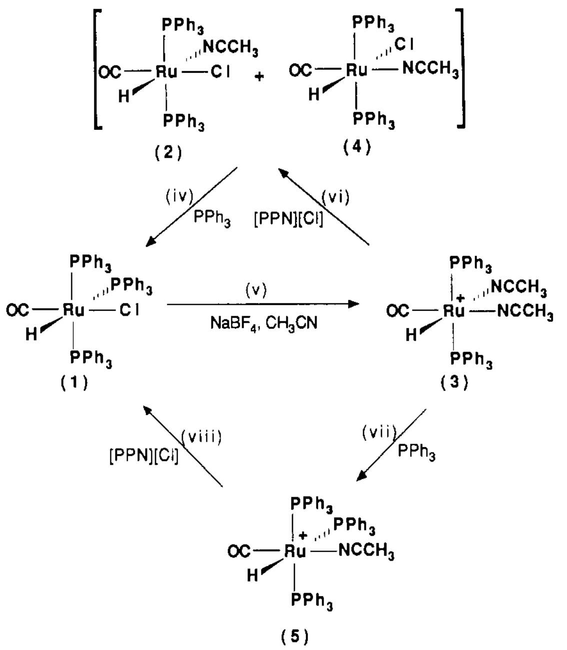
In $CD_3CN$ the complex is insoluble, but if such a suspension is heated to 65 °C for 10–15 min, a clear yellow solution is obtained. The high-field $^1H$ NMR spectrum of this solution consists of three triplets of relative integrals 2:5:3, which can be ascribed to the formation of three new hydrido–bis(phosphine) species **2′**, **3′**, and **4′** (Table I). The $^{31}P\{^1H\}$ NMR spectrum shows three corresponding singlets (Table I) with the same integral ratios, also consistent with the presence of three species containing two equivalent phosphine ligands, plus a signal at −6.0 ppm due to free triphenylphosphine. The composition of the mixture does not change on prolonged heating, indicating that an equilibrium is rapidly attained.

These results can be interpreted in terms of the reaction sequence shown in Scheme II: On heating **1** in $CD_3CN$, the phosphine trans to the hydride is displaced by the nitrogen base to yield **2′** (reaction i); this is in agreement with the known chemistry of **1**, which shows that this is the most substitution-labile ligand.[6] Subsequent chloride displacement by $CD_3CN$ from **2′** yields the cationic bis(acetonitrile) species **3′** (reaction ii); this type of halide abstraction by nitriles is known for related complexes.[21] Recoordination of $Cl^-$ to **3′** in a position cis to H produces **4′**, a geometrical isomer of **2′** (reaction iii).

These three complexes coexist in solution at room temperature, but on cooling of the mixture to −20 °C overnight, the two neutral isomers **2′** and **4′** cocrystallize, while **3′** remains in solution.

Further support for this interpretation comes from the following set of independent experiments, summarized in Scheme III: A mixture of the analogous nondeuterated complexes **2** and **4** was obtained from a preparative scale reaction of **1** with $CH_3CN$ and crystallized at −20 °C as described above. Addition of $PPh_3$ to a $CD_2Cl_2$ solution of this mixture regenerates the $^1H$ and $^{31}P$ NMR spectra of **1**, plus a signal corresponding to free acetonitrile (reaction iv). If **1** is reacted with $CH_3CN$ in the presence of $NaBF_4$, the only species observed by NMR spectroscopy is the bis(acetonitrile) cation **3**, which can be isolated pure in high yields as the $BF_4^-$ salt (reaction v). Addition of $[(PPh_3)_2N][Cl]$ to a solution of pure **3** produces the combined spectra of **2** + **4** (reaction vi). Subsequent addition of $PPh_3$ yields **1** essentially quantitatively (reaction iv). If, on the other hand, 1 equiv of $PPh_3$ is added to a $CD_2Cl_2$ solution of **3**, $^1H$ and $^{31}P$ patterns very similar to those of **1** (but displaced about 1 ppm to higher fields in the $^1H$ spectrum) are observed (Table I), consistent with the formation of a cationic tris(triphenylphosphine) complex $[RuH(CO)(NCMe)(PPh_3)_3]^+$ (**5**) (reaction vii). Addition of $[(PPh_3)_2N][Cl]$ to **5** regenerates **1** (reaction viii). Complex **5** can also be isolated in a pure form as the $BF_4$ salt, from a preparative scale reaction (vide infra).

**Scheme III**



**[RuH(CO)(NCMe)$_2$(PPh$_3$)$_2$][BF$_4$] (3).** Complex **3** may be isolated in high yields from the reaction of **1** with $NaBF_4$ in acetonitrile. This compound is an air-stable, white crystalline material that melts with decomposition at 190–191 °C. It is very soluble in acetonitrile, acetone, chloroform, and dichloromethane and moderately soluble in toluene, tetrahydrofuran, and alcohols. The conductivity of a $10^{-3}$ M solution of **3** in nitromethane was 68.5 $cm^2\ \Omega^{-1}\ mol^{-1}$ (or 80.1 $cm^2\ \Omega^{-1}\ mol^{-1}$ at infinite dilution), which corresponds well to a 1:1 electrolyte.[22] The IR spectrum of **3** (KBr disk) shows a medium-intensity band at 2015 $cm^{-1}$ due to the Ru–H stretch, a strong $\nu_{CO}$ band at 1930 $cm^{-1}$, and a strong band at 1080 $cm^{-1}$ characteristic of the $BF_4^-$ anion.

The $^1H$ and $^{31}P\{^1H\}$ NMR spectra (Table I) are consistent with the stereochemistry shown as **3**, containing one hydride ligand cis to two equivalent triphenylphosphines.

Some aspects of the coordination chemistry of **3** have been studied, as summarized in Scheme I. NMR data for all the new compounds (see Table I) are in agreement with the proposed structures.

Complex **3** reacts with a variety of Lewis bases such as $PPh_3$, $P(OMe)_3$, 1,2-bis(diphenylphosphino)ethane (diphos), pyridine, and CO, by replacement of the acetonitrile ligands, to yield complexes **5**–**11**. Generally the nitrile trans to the hydride is readily displaced at room temperature, while the second acetonitrile is only displaced on warming above 50 °C. This is a very interesting property, since the 18-electron complex **3** may serve as a source of a 16- or a 14-electron species depending on the reaction temperature.

The cation **3** also reacts readily with anions such as $Cl^-$, $I^-$, and $OAc^-$ to generate the corresponding neutral derivatives (see Scheme I and Table I). The carbonylate anion $[Co(CO)_4]^-$ also

---

(21) Treichel, P. M.; Vicenti, P. J. *Inorg. Chem.* **1985**, *24*, 228.

(22) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81. Bogges, R. K.; Zatko, D. A. *J. Chem. Educ.* **1975**, *52*, 649.

reacts instantaneously with **3** to yield the heterobimetallic complex [Ru(CO)$_3$(PPh$_3$)($\mu$-PPh$_2$)Co(CO$_3$)] (**12**), characterized by X-ray diffraction.[23] This compound was independently synthesized and characterized crystallographically by Regragui et al.[24]

**Catalytic Hydroformylation of Hex-1-ene by Complex 3.** The hydroformylation of olefins by use of neutral ruthenium phosphine complexes has been studied in some detail.[25] The activities and selectivities reported are much lower than those observed for the industrially used RhH(CO)(PPh$_3$)$_3$, which is known to dissociate in solution into the active species RhH(CO)(PPh$_3$)$_2$.[26]

The reactivity of the cation **3** reported above shows that in solution, at temperatures above 50 °C, this complex may be considered a source of the fragment "[RuH(CO)(PPh$_3$)$_2$]$^{+}$", presumably isoelectronic and isostructural with the rhodium system. It thus seemed interesting to investigate the catalytic properties of **3** for this commercially important reaction.

The results of hydroformylating hex-1-ene with **3** in toluene solution are collected in Table II. The complex shows a catalytic activity comparable to those observed for neutral ruthenium compounds.[25] At 120 °C and 100 bar H$_2$/CO (1:1) an important proportion of olefin isomerization and hydrogenation products was obtained; both aldehydes and alcohols were produced with low linear to branched (*n*/*i*) ratios (ca. 1.5). At 150 °C and 100 bar H$_2$/CO (1:2), complete conversion was obtained with higher selectivities for olefin hydroformylation with respect to isomerization or hydrogenation; the main products in this case were the corresponding alcohols, which is not surprising in view of the high efficiency of ruthenium phosphine complexes as catalysts for the reduction of aldehydes.[16] The *n*/*i* ratio, however, is even lower under these conditions; addition of PPh$_3$, PCy$_3$, or P(OPh)$_3$ did not improve the proportion of linear products but caused adverse effects on the hydroformylation rates. After the catalytic runs, the main species recovered was [RuH(CO)$_3$(PPh$_3$)$_2$][BF$_4$].

## Experimental Section

Manipulations were routinely carried out under dry nitrogen or argon by using Schlenk techniques or a drybox. Solvents were purified by conventional procedures; other reactants were of analytical grade and were generally used without further purification. IR and NMR spectra were recorded on Perkin-Elmer 1310 and Bruker WP 60 or AM 300 spectrometers, respectively. Complex **1** was prepared according to the literature method.[2] Elemental analyses were done by Mikroanalytisches Labor Pascher.

**RuHCl(CO)(NCMe)(PPh$_3$)$_2$ (2 + 4).** Complex **1** (250 mg, 0.26 mmol) and freshly distilled and degassed MeCN (30 mL) were rapidly stirred under reflux under N$_2$ for 1 h, after which a pale yellow solution was obtained. The mixture was evaporated under vacuum to about one-third of its volume and cooled to −20 °C to coprecipitate the isomeric complexes **2** + **4** as an air-sensitive white solid, which was filtered out and dried in vacuo (52% yield). IR: $\nu_{Ru-H}$ 2000 (m) and $\nu_{CO}$ 1930 (vs) cm$^{-1}$.

**[RuH(CO)(NCMe)$_2$(PPh$_3$)$_2$][BF$_4$] (3).** To a suspension of complex **1** (3.0 g, 3.15 mmol) in MeCN (200 mL) was added NaBF$_4$ (348 mg, 3.18 mmol), and the mixture was gently refluxed until the solution turned pale yellow (ca. 1 h). The solution was filtered and evaporated to dryness; the resulting white solid was washed twice with diethyl ether, redissolved in the minimum amount of dichloromethane, and precipitated by slow addition of *n*-pentane, to obtain white crystals of **3**, which were washed with diethyl ether and pentane and dried in vacuo (90% yield). IR: $\nu_{Ru-H}$ 2015 (m), $\nu_{CO}$ 1930 (vs), and $\nu_{B-F}$ 1080 (s) cm$^{-1}$. Mp: 190–191 °C (dec). These data coincide with those reported by Roper for the analogous perchlorate complex.[19]

**[RuH(CO)(NCMe)(PPh$_3$)$_3$][BF$_4$] (5).** To a solution of complex **3** (1.0 g, 1.2 mmol) in dichloromethane (50 mL) was added triphenylphosphine (0.32 g, 1.2 mmol); the mixture was vigorously stirred at ambient temperature for 1–2 h and then evaporated to ca. 10 mL. Slow addition of *n*-pentane caused precipitation of **5** as a white solid, which was filtered out, washed with diethyl ether and *n*-pentane, and dried in vacuo (80% yield). Anal. Calcd for RuC$_{57}$H$_{49}$NBF$_4$OP$_3$·CH$_2$Cl$_2$: C, 61.7; H, 4.5; N, 1.2. Found: C, 62.3; H, 4.7; N, 1.4. IR: $\nu_{Ru-H}$ 1988 (m) and $\nu_{CO}$ 1950 (vs) cm$^{-1}$. Mp: 173 °C.

**{RuH(CO)(NCMe)(PPh$_3$)$_2$[P(OMe)$_3$]}{BF$_4$} (6).** To a solution of complex **3** (150 mg, 0.18 mmol) in dichloromethane (20 mL) was added trimethylphosphite (1 mL), and the mixture was vigorously stirred at ambient temperature for 1 h. The solution was evaporated to ca. one-third of its volume, after which the complex began to precipitate. Addition of *n*-pentane completed precipitation of complex **6** as a white crystalline solid, which was washed with diethyl ether and *n*-pentane and dried in vacuo (75% yield); mp 142 °C. Anal. Calcd for RuC$_{42}$H$_{43}$NBF$_4$O$_4$P$_3$: C, 55.6; H, 4.8; N, 1.5. Found: C, 54.9; H, 4.8; N, 1.4. IR: $\nu_{Ru-H}$ 1905 (m) and $\nu_{CO}$ 1962 (vs) cm$^{-1}$.

**[RuH(CO)(NCMe)(PPh$_3$)$_2$(diphos)][BF$_4$] (7).** Complex **3** (200 mg, 2.4 mmol) and diphos (100 mg, 2.5 mmol) were dissolved in dichloromethane (30 mL), and the mixture was vigorously stirred at ambient temperature for 1 h. The solution was then concentrated to a small volume, and *n*-pentane was slowly added to precipitate complex **7** as an off-white solid, which was filtered out and dried in vacuo (87% yield). Anal. Calcd for RuC$_{65}$H$_{58}$NBF$_4$OP$_4$·0.5CH$_2$Cl$_2$: C, 64.3; H, 4.8; N, 1.1. Found: C, 64.6; H, 5.0; N, 1.0. IR: $\nu_{CO}$ 1944 (vs) cm$^{-1}$. Mp: 125 °C.

**[RuH(CO)(py)$_2$(PPh$_3$)$_2$][BF$_4$] (9).** To a solution of complex **3** (156 mg, 0.19 mmol) in chloroform (30 mL) was added an excess of pyridine (1 mL). The solution was vigorously stirred and heated to 60 °C for 3 h. After cooling to ambient temperature, the solution was concentrated to a small volume, and complex **9** was precipitated as a cream-colored solid by addition of *n*-pentane. The solid was washed with diethyl ether and *n*-pentane and dried in vacuo (82% yield). IR: $\nu_{Ru-H}$ 2015 (m) and $\nu_{CO}$ 1925 (vs) cm$^{-1}$. Mp: 168 °C. The spectral data for this complex are very similar to those previously reported for the perchlorate salt of this cation.[20a]

**[RuH(CO)$_2$(NCMe)(PPh$_3$)$_2$][BF$_4$] (10).** A slow stream of CO was bubbled through a solution of complex **3** (280 mg, 0.34 mmol) in dichloromethane (50 mL) with vigorous stirring at ambient temperature. The solution was concentrated to a small volume, and *n*-pentane was added to precipitate complex **10** as a white solid, which was filtered out and dried in vacuo (80% yield). Anal. Calcd for RuC$_{40}$H$_{34}$NBF$_4$O$_2$P$_2$: C, 59.3; H, 4.2; N, 1.7. Found: C, 58.5; H, 4.2; N, 1.9. IR: $\nu_{CO}$ 2003 (vs) and 2062 (vs) cm$^{-1}$.

**[RuH(CO)$_3$(PPh$_3$)$_2$][BF$_4$] (11).** A slow stream of CO was bubbled through a solution of complex **3** (280 mg, 0.34 mmol) in chloroform/toluene (50 mL) under reflux for 2 h. After cooling to ambient temperature, the solution was concentrated and *n*-pentane was added to precipitate complex **11** as a white solid, which was washed with diethyl ether and *n*-pentane and dried in vacuo (60% yield). IR: $\nu_{CO}$ 1990 (vs, br) and 2052 (vs) cm$^{-1}$.

**RuHI(CO)(NCMe)(PPh$_3$)$_2$ (12).** To a solution of complex **3** (200 mg, 2.4 mmol) in dichloromethane (40 mL) was added [(PPh$_3$)$_2$N][I] (2.4 mmol), and the mixture was stirred at ambient temperature for 1 h. The solution was concentrated to a small volume, and *n*-pentane was added to precipitate **12** as a pinkish white solid, which was filtered out and washed with cold methanol, water, methanol, and *n*-pentane (75% yield). Anal. Calcd for RuC$_{39}$H$_{34}$NIOP$_2$: C, 56.9; H, 4.2; N, 1.7. Found: C, 57.4; H, 4.1; N, 1.7. IR: $\nu_{Ru-H}$ 2020 (m) and $\nu_{CO}$ 1926 (vs) cm$^{-1}$.

**[Ru(CO)$_3$(PPh$_3$)($\mu$-PPh$_2$)Co(CO)$_3$] (13).** To a solution of [(PPh$_3$)$_2$N][Co(CO)$_4$] (226 mg, 0.32 mmol) in dichloromethane (30 mL) was slowly added a solution of complex **3** in dichloromethane (10 mL); an intense red coloration was immediately observed. The solution was stirred for 1 h at ambient temperature, after which it was evaporated to dryness. The product was chromatographed on a silica plate by using a 1:1 mixture of dichloromethane–hexane, and complex **13** was extracted from the support with dichloromethane and recrystallized by slow evaporation of a diethyl ether solution to yield red crystals adequate for X-ray diffraction (30% yield). Anal. Calcd for RuCoC$_{36}$H$_{25}$O$_6$P$_2$·0.5CH$_2$Cl$_2$: C, 53.6; H, 3.2; P, 7.6. Found: C, 53.3; H, 3.3; P, 7.8. IR: $\nu_{CO}$ 1932 (s), 1998 (vs), and 2076 (vs) cm$^{-1}$. $^{31}$P NMR: 53 (s) and 15 (s) ppm.

**Catalytic Hydroformylation of Hex-1-ene.** Complex **3** (82 mg, 0.1 mmol), hex-1-ene (1.2 mL, 10 mmol), toluene (50 mL), and a stirring bar were placed in a glass-lined stainless steel autoclave. The autoclave was flushed with hydrogen, charged with H$_2$/CO to the desired pressure, and subsequently introduced in an electric oven preheated to the required temperature; stirring was immediately commenced. After 20 h of reaction the autoclave was rapidly cooled in an ice bath, the excess pressure was released, and the products were analyzed by gas chromatography using a Varian 3700 instrument fitted with a flame ionization detector and a 30-m 10% SE-30 column and coupled to a Varian VISTA CDS-401 automatic data system.

**Acknowledgment.** We thank the FGMA for a Graduate Fellowship to M.R. and V. Herrera for technical aid.

---

(23) Braga, D. Personal communication.

(24) Regragui, R.; Dixneuf, P. H.; Taylor, N. J.; Carty, A. J. *Organometallics* **1986**, *5*, 1.

(25) Sãnchez-Delgado, R. A.; Bradley, J. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 399.

(26) Masters, C. *Homogeneous Transition Metal Catalysis. A Gentle Art.* Chapman and Hall: New York, 1981.