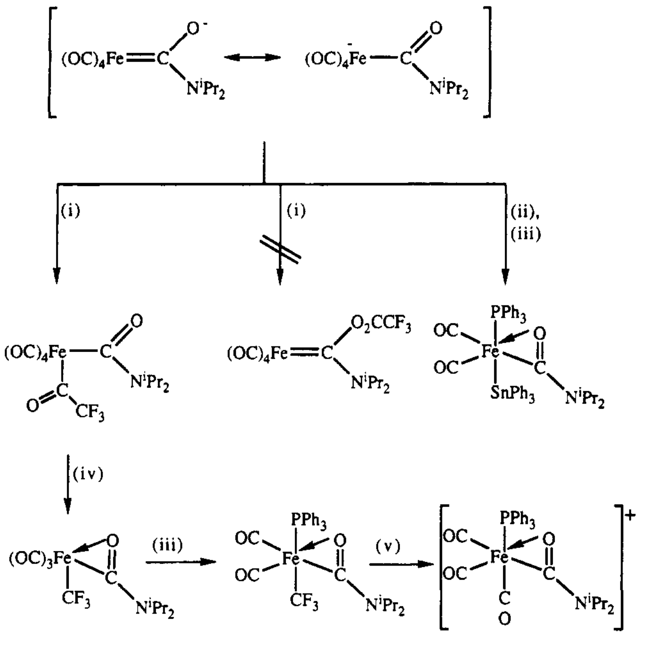
Scheme I[a]



[a] Legend: (i) $(CF_3CO)_2O$; (ii) Ph_3SnCl; (iii) PPh_3; (iv) –CO; (v) HBF_4/H_2O, –3HF.

treating the carbamoylate with the soft electrophile Ph_3SnCl followed by triphenylphosphine provides the stannyl complex $[Fe(SnPh_3)\{\eta^2\text{-}C(=O)N^iPr_2\}(CO)_2(PPh_3)]$ (Sn trans to P)[12] further support this. The divergence in reactivity between the carbamoylates $[Cr\{C(=O)N^iPr_2\}(CO)_5]^-$ and $[Fe\{C(=O)N^iPr_2\}(CO)_4]^-$ is presumably due in part to the increased accessibility of the 5-coordinate iron center toward electrophiles relative to the 6-coordinate chromium complex.

We are currently investigating the versatility of the conveniently accessible (carbamoyl)carbonylferrate $[Fe\{\eta^1\text{-}C(=O)N^iPr_2\}(CO)_4]^-$ in reactions with other electrophiles which provide an expedient entry into the carbamoyl chemistry of iron(II).

Supplementary Material Available: Tables of crystal data and data collection and refinement details, atomic positional and thermal parameters, and bond lengths and angles for $[Fe(CF_3)\{\eta^2\text{-}C(=O)N^iPr_2\}(CO)_2(PPh_3)]$ (8 pages). Ordering information is given on any current masthead page.

OM9107855

---

(12) Data for $[Fe(SnPh_3)\{\eta^2\text{-}C(=O)N^iPr_2\}(CO)_2(PPh_3)]$: IR ($CH_2Cl_2$) 1979 s, 1908 vs [$\nu$(CO)], 1585 m (acyl); FAB-MS m/z 851 ($[M]^+$), 795 ($[M - 2CO]^+$), 720 ($[M - 2CO - C_6H_5]^+$), 668 ($[Fe(PPh_3)(SnPh_3)]$), 563 ($[M - PPh_3 - CO]^+$), 535 ($[M - PPh_3 - 2CO]^+$), 351 ($[SnPh_3]^+$), 318 ($[FePPh_3]^+$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C) δ 218.0 [d (br), Fe(CO)], 196.7 [d, OCN^iPr_2, 12.9 Hz], 145.7 [d, $C^1(SnC_6H_5)$, J(PC) 5.1 Hz, J(SnC) ca. 258 Hz, $J(^{119}SnC/^{117}SnC)$ not resolved], 137.2 [$C^{2,6}(SnC_6H_5)$, J(SnC) ca. 32.9 Hz], 133.8 [d, $C^1(PC_6H_5)$, J(PC) 35.0 Hz], 133.4 [d, $C^{2,6}(PC_6H_5)$, J(PC) 10.5], 129.7, 127.1 [s × 2, $C^4(PC_6H_5)$ and $C^4(SnC_6H_5)$], 128.2 [d, $C^{3,5}(PC_6H_5)$, J(PC) 9.1], 127.4 [$C^{3,5}(SnC_6H_5)$, J(SnC) ca. 37.5 Hz], 54.4, 47.5 [s × 2, $NCHMe_2$], 20.7, 20.1 [br, $NCH(CH_3)_2$]; ^{31}P NMR ($CDCl_3$, 25 °C) δ 53.8 [J ($P^{11x,y}Sn$) 637, 608 Hz]. Anal. Calcd for $C_{45}H_{44}FeNO_3PSn{\cdot}CH_2Cl_2$: C, 59.0; H, 4.9; N, 1.7. Found: C, 59.8; H, 5.0; N, 1.4.

Water-Soluble Organometallic Compounds. 2. Catalytic Hydrogenation of Aldehydes and Olefins by New Water-Soluble 1,3,5-Triaza-7-phosphaadamantane Complexes of Ruthenium and Rhodium

Donald J. Darensbourg,* Ferenc Joo,† Michael Kannisto, Agnes Katho,† and Joseph H. Reibenspies

Department of Chemistry, Texas A&M University, College Station, Texas 77843

Received December 6, 1991

Summary: Water-soluble phosphine complexes of ruthenium(II) and rhodium(I) have been prepared by the reduction of $RuCl_3$ and $RhCl_3$ in ethanol in the presence of the air-stable phosphine 1,3,5-triaza-7-phosphaadamantane (**1**). The complex $RuCl_2(PTA)_4$ (**2a**) and its protonated analog $RuCl_2(PTA)_4{\cdot}2HCl$ (**2b**) have been characterized by X-ray crystallography. Similarly, the *cis*-bis(phosphine) complex $RhCl(PTA)_2{\cdot}2HCl$, derived from the protonation of $RhCl(PTA)_3$ by HCl, has been characterized by X-ray crystallography. The water-soluble ruthenium phosphine derivative **2a** is catalytically quite active for the conversion of unsaturated aldehydes to unsaturated alcohols using a biphasic aqueous/organic medium with formate as the source of hydrogen. By way of contrast, under similar conditions $RhCl(PTA)_3$ is a very active catalyst for olefin hydrogenation.

Much attention has been focused recently on reactions catalyzed by organometallic reagents in aqueous or biphasic aqueous–organic media.[1] Despite the impressive progress in the synthesis of organometallic complexes

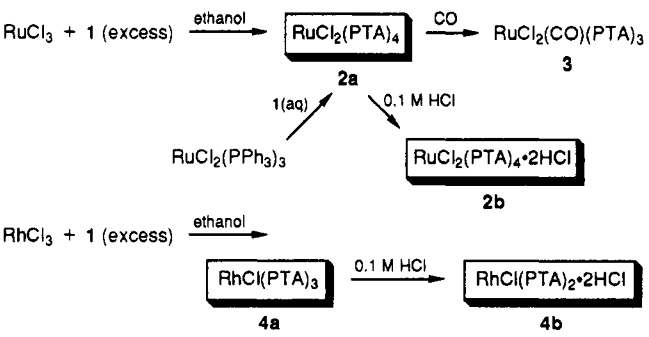
---

† Permanent address: Institute of Physical Chemistry, Kossuth Lajos University, P.O. Box 7, Debrecen, H-4010 Hungary.

(1) (a) Herrmann, W. A.; Kulpe, J. A.; Kellner, J.; Riepl, H.; Bahrmann, H.; Konkol, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 391. (b) Herrmann, W. A.; Kulpe, J. A.; Bahrmann, H.; Konkol, W. *J. Organomet. Chem.* **1990**, *389*, 85. (c) Herrmann, W. A.; Kulpe, J. A.; Bahrmann, H.; Konkol, W. *J. Organomet. Chem.* **1990**, *389*, 103. (d) Kuntz, E. G. *CHEMTECH* **1987**, *17*, 570. (e) Mignani, G.; Morel, D.; Colleuille, Y. *Tetrahedron Lett.* **1985**, *26*, 6337. (f) Toth, Z.; Joo, F.; Beck, M. T. *Inorg. Chim. Acta* **1980**, *42*, 153. (g) Joo, F.; Toth, Z. *J. Mol. Catal.* **1980**, *8*, 369. (h) Borowski, A. F.; Cole-Hamilton, D. J.; Wilkinson, G. *Nouv. J. Chim.* **1978**, *2*, 137. (i) Joo, F.; Beck, M. T. *Magy. Kem. Foly.* **1973**, *79*, 189. (j) Okano, T.; Uchida, I.; Nakagaki, T.; Konishi, H.; Kiji, J. *J. Mol. Catal.* **1989**, *54*, 65. (k) Labinger, J. A.; Herring, A. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 5628. (l) McGrath, D. V.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 3611. (m) Wai, J. S. M.; Marko, I.; Svendsen, J. S.; Finn, M. G.; Jacobsen, E. N.; Sharpless, K. B. *J. Am. Chem. Soc.* **1989**, *111*, 1123. (n) Halpern, J. *J. Organomet. Chem.* **1980**, *200*, 133. (o) Casalnuovo, A. L.; Calabrese, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 4324. (p) Herrmann, W. A.; Thiel, W. R.; Kuchler, J. G.; Behm, J.; Herdtweck, E. *Chem. Ber.* **1990**, *123*, 1963. (q) Toth, I.; Hanson, B. E.; Davis, M. E. *Catal. Lett.* **1990**, *5*, 183. (r) Toth, I.; Hanson, B. E.; Davis, M. E. *J. Organomet. Chem.* **1990**, *397*, 109. (s) Horvath, I. T.; Kastrup, R. V.; Oswald, A. A.; Mozeleski, E. J. *Catal. Lett.* **1989**, *2*, 85. (t) Sinou, D. *Bull. Soc. Chim. Fr.* **1987**, 480. (u) Russell, M. J. H. *Platinum Met. Rev.* **1988**, *32*, 179. (v) Smith, R. T.; Ungar, R. K.; Sanderson, L. J.; Baird, M. C. *Organometallics* **1983**, *2*, 1138. (w) Markiewicz, M. K.; Baird, M. C. *Inorg. Chim. Acta* **1986**, *113*, 95.

0276-7333/92/2311-1990$03.00/0

Scheme I



which are dissolvable in water, the number of available water-soluble ligands is limited. For example, most investigations of metal phosphine complexes involve the sulfonated phosphine ligands (*m*-sulfophenyl)diphenylphosphine, tris(*m*-sulfophenyl)phosphine, and various sulfonated chiral diphosphines.[2] Hence, there is a need for a wider variety of water-soluble phosphine ligands, covering a range of steric and electronic properties. In this regard 1,3,5-triaza-7-phosphaadamantane (PTA), a small, air-stable, nonionic, aliphatic phosphine first prepared by Daigle et al.[3] and structurally characterized as its molybdenum carbonyl complex by Darensbourg and co-workers,[4] has been suggested for use as a water-soluble ligand in catalytic processes.[5] Herein we report the first synthesis, characterization, and catalytic activity of water-soluble PTA (1) complexes of ruthenium and rhodium.

Addition of 6 equiv of 1 to hydrated $RuCl_3$ in refluxing ethanol affords a slightly greenish yellow precipitate of the formula $RuCl_2(PTA)_4$ (**2a**) in quantitative yield. The same complex can be obtained by extracting toluene or dichloromethane solutions of $RuCl_2(PPh_3)_3$ with an aqueous solution of 1 (the solubility of 1 in H_2O is 1.5 M). **2a** is soluble in alkaline or neutral aqueous solutions (>0.1 M) but is only sparingly soluble in ethanol and 2-methoxyethanol and is insoluble in nonpolar organic solvents. When the extraction is done with a 0.1 M HCl solution of 1, or **2a** is recrystallized from dilute HCl, the diprotonated product (**2b**) is obtained.[6] Further reaction of **2a** with CO in 2-methoxyethanol afforded the carbonyl species **3**, which displayed a ν(CO) band at 1987 cm^{-1}.[7] In an analogous manner the reaction of $RhCl_3$ with an excess of 1 in refluxing ethanol led to an orange-yellow precipitate of the rhodium(I) derivative **4a**, which when recrystallized from HCl results in the formation of **4b**. These reactions are summarized in Scheme I.

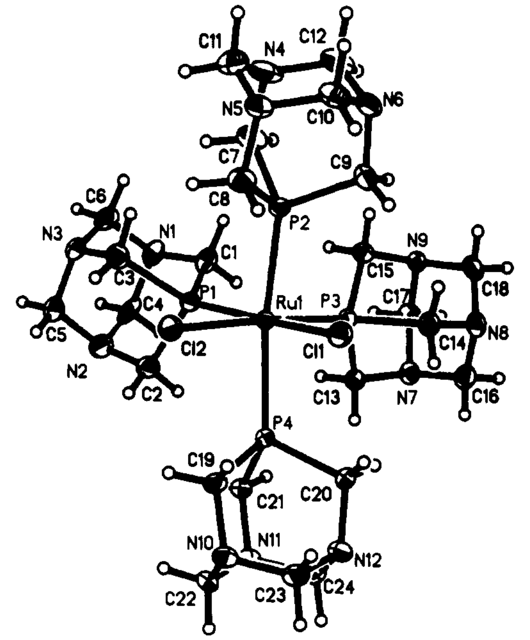


Figure 1. ORTEP view of $RuCl_2(PTA)_4$ (**2a**), with ellipsoids drawn at the 50% probability level. Pertinent bond lengths (Å) and bond angles (deg) are as follows: Ru1–Cl1 = 2.488 (2), Ru1–Cl2 = 2.503 (2), Ru1–P1 = 2.267 (2), Ru1–P2 = 2.351 (2), Ru1–P3 = 2.252 (2), Ru1–P4 = 2.388 (2); Cl1–Ru1–Cl2 = 84.2 (1), P2–Ru1–P4 = 164.8 (1), P1–Ru1–P3 = 96.5 (1).

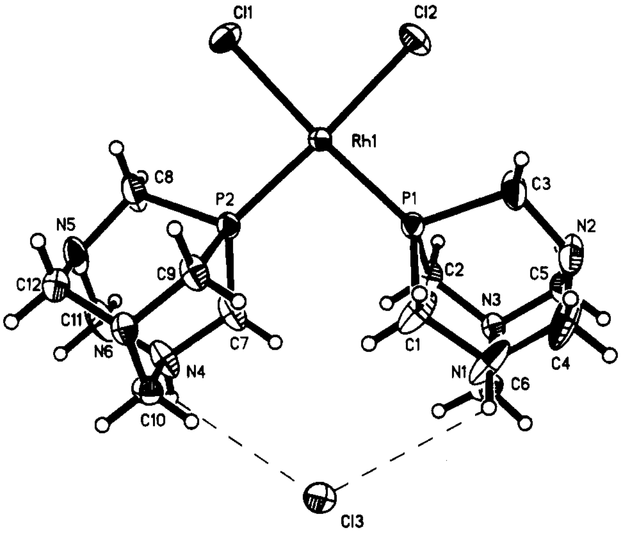


Figure 2. ORTEP view of $RhCl(PTA)_2{\cdot}2HCl$ (**4b**), with ellipsoids drawn at the 50% probability level. Pertinent bond lengths (Å) and bond angles (deg) are as follows: Rh1–Cl1 = 2.407 (2), Rh1–Cl2 = 2.407 (2), Rh1–P1 = 2.188 (2), Rh1–P2 = 2.187 (2); Cl1–Rh1–Cl2 = 86.8 (1), P1–Rh1–P2 = 94.2 (1).

The ruthenium derivatives **2a** and **2b** and the rhodium derivative **4b** have been characterized by single-crystal X-ray diffraction studies.[8] ORTEP diagrams of **2a** and **4b**

---

(2) Amrani, Y.; Lecomte, L.; Sinou, D.; Bakos, J.; Toth, I.; Heil, B. *Organometallics* **1989**, *8*, 542.

(3) Daigle, D. J.; Pepperman, A. B., Jr.; Vail, S. L. *J. Heterocycl. Chem.* **1974**, *17*, 407.

(4) (a) Darensbourg, M. Y.; Daigle, D. *Inorg. Chem.* **1975**, *14*, 1217. (b) DeLerno, J. R.; Trefonas, L. M.; Darensbourg, M. Y.; Majeste, R. J. *Inorg. Chem.* **1976**, *15*, 816. A later publication dealing with the structure of the free ligand has appeared: Fluck, E.; Forster, J. E.; Weidlein, J.; Hadicke, E. *Z. Naturforsch.* **1977**, *32B*, 499.

(5) Fisher, K. J.; Alyea, E. C.; Shahnazarian, N. *Phosphorus, Sulfur Silicon Relat. Elem.* **1990**, *48*, 37.

(6) The preparation of **2a** and **2b** was as follows: To a stirred, warm slurry of PTA (1.89 g, 12.0 mmol) in 50 mL of 96% ethanol was added under nitrogen a warm solution of $RuCl_3{\cdot}3H_2O$ (0.52 g, 2.0 mmol) in 25 mL of ethanol. The resulting mixture changed color in a few minutes from deep brown-red to light green-brown and was refluxed under nitrogen for 2 h. After the mixture was cooled to ambient temperature, the resultant solid was filtered and washed with ethanol and acetone. The product, **2a**, was dried under vacuum to afford 1.6 g (98% yield) of a yellow powder. X-ray-quality crystals were obtained from a saturated water solution. ^1H NMR (200 MHz): δ 4.67 (broad singlet) and δ 4.40 (broad singlet), which correspond to the methylene units between two nitrogens and between a nitrogen and a phosphorus, respectively. Concomitantly, the phosphines are all equivalent in the ^{31}P NMR spectrum, exhibiting a resonance at −47.3 ppm, as compared to −89.8 ppm in 1. Anal. Calcd for $C_{24}H_{48}N_{12}P_4Cl_2Ru$ (M_r 800.6): C, 36.01; H, 6.04; Cl, 8.86. Found: C, 35.95; H, 6.20; Cl, 8.88. A solution of 100 mg of **2a** in 1.0 mL of 0.1 M HCl, when layered with 2.5 mL of ethanol, afforded X-ray-quality yellow crystals of **2b**.

(7) For the triphenylphosphine analog of this complex, see: (a) Halpern, J.; James, B. R.; Kemp, A. L. W. *J. Am. Chem. Soc.* **1966**, *88*, 5142. (b) Poddar, R. K.; Agarwala, U. *Indian J. Chem.* **1971**, *9*, 477.

(8) Many of the details of these X-ray structure analyses may be found in the supplementary material.

Table I. Reduction of Unsaturated Substrates by Hydrogen Transfer Catalyzed by 2a[a]

substrate (amt, mmol)	conversion, %[b]
benzaldehyde (4.92)	64.0
	0.40[c]
	7.1[d]
	95.1[e]
4-methylbenzaldehyde (4.24)	23.6
4-methoxybenzaldehyde (4.11)	26.7
4-bromobenzaldehyde (1.35)	16.3
2-hydroxybenzaldehyde (4.69)	
cinnamaldehyde[f] (3.96)	21.2
1-hexanal (4.16)	23.0

[a] Conditions: 0.0625 mmol of **2a**, 5 mL of chlorobenzene, and 5 mL of 5 M HCO_2Na in water; 80 °C; reaction time 3 h. The high formate concentration ensured only slight pH changes around 7.5.[12] [b] By GC analysis. [c] Reaction carried out in the presence of a 10-fold excess of **1**. [d] Reaction carried out in the presence of an atmosphere of CO. [e] $RuCl_2(PTA)_3$ prepared by extraction of a CH_2Cl_2 solution of $RuCl_2(PPh_3)_3$ with an aqueous solution of **1**. The composition is based on spectrophotometric extraction experiments. [f] 100% selective toward cinnamyl alcohol.

are provided in Figures 1 and 2. Both **2a** and **2b** consist of ruthenium in an octahedral environment with cis Cl ligands. In the two derivatives the Ru–P bond lengths for the phosphine ligands trans to Cl are shorter than the corresponding values trans to phosphine; e.g., in **2a** these Ru–P distances are 2.260 [2] and 2.370 [2] Å, respectively. In **2b** the mutually trans phosphine ligands are protonated at one of the nitrogen atoms, with these quaternary nitrogens possessing N–C bond distances slightly longer than their tertiary counterparts, 1.518 [7] vs 1.461 [7] or 1.474 [7] Å.[9] The free chloride ions in **2b** are hydrogen-bonded to the protonated nitrogen atoms, with a N–H···Cl distance of 3.050 Å being observed. These chloride ions are each additionally solvated by two water molecules. Furthermore, one nitrogen atom from each of the nonprotonated phosphine ligands is hydrogen-bonded to a water molecule with a N···H–O distance of 2.930 Å. The geometry of **4b** is that of a square-planar anionic Rh(I) derivative with two cis phosphine ligands and two cis chloride ligands. Both phosphine ligands are monoprotonated at nitrogen. Charge balancing is accomplished by the presence of an extra chloride ion located in the lattice equidistant between the two phosphine ligands. Although $Rh(CO)_2X_2^-$ anions are well-known,[10a] phosphine analogs of these derivatives are rare.[10b]

The water-soluble ruthenium phosphine derivative **2a** is catalytically quite active for the conversion of unsaturated aldehydes to unsaturated alcohols using a biphasic aqueous–organic medium with formate as the source of hydrogen.[11,12] For example, the initial turnover frequency for benzaldehyde to benzyl alcohol was 22 h^{-1} at 80 °C. The results for the reduction of various aldehydes by **2a** are summarized in Table I. In all reactions the organic phase remained clear and colorless, indicative of no significant quantity of ruthenium complex in this phase. This was further verified by the UV–vis spectrum of the organic phase, where no ruthenium complex was detected. A strongly coordinating substituent in the position ortho to the aldehyde functionality, i.e. 2-hydroxybenzaldehyde, inhibits the catalytic reaction completely.[12] Included in this investigation was cinnamaldehyde, where *selective* reduction of the aldehyde functionality occurred with only cinnamyl alcohol being produced. These reductions are greatly inhibited by addition of a 10-fold excess of **1** or an atmosphere of carbon monoxide. Concomitantly, when only three PTA ligands are available per ruthenium, the rate of reduction is enhanced, with an initial turnover frequency of 32 h^{-1}. The aqueous catalytic phase was recycled several times with no significant loss of catalytic activity. However, when using NaO_2CH as a hydrogen source, it was necessary to remove the Na_2CO_3 byproduct after every other cycle to maintain the reaction rate.

Similarly, **2a** is a catalyst for the selective reduction of unsaturated aldehydes to unsaturated alcohols using hydrogen gas. However, because of the low solubility of H_2 in water this is a very slow process at atmospheric pressure, with higher pressures of H_2 (400 psi) being needed for modest conversion rates.[13] For example, **2a** in the presence of 1 atm of H_2 in water–chlorobenzene solution leads to a 2.6% conversion of benzaldehyde in 3 h, whereas under a 400 psi pressure of H_2 a 45.9% conversion is noted in 5 h for a phosphate-buffered reaction mixture (pH 8).

By way of contrast, **4a** is an active catalyst for olefin hydrogenation and is almost completely inactive for the hydrogenation of the aldehyde functionality. Consequently, cinnamaldehyde could be selectively hydrogenated to dihydrocinnamaldehyde (3-phenylpropionaldehyde) with **4a**, with an initial turnover frequency of 82 h^{-1} at 50 °C. As with **2a**, **4a** can utilize HCO_2Na/H_2O or hydrogen gas as the source of hydrogen. Allylbenzene is also rapidly hydrogenated by **4a**, and the reaction is accompanied by extensive isomerization to *cis*- and (mainly) *trans*-propenylbenzene.[13] A case in point is that at an allylbenzene conversion of 97.1%, the yield of *trans*-propenylbenzene is 44.5%. The isomerization was even more pronounced with HCO_2Na than with H_2, where the overall reaction is somewhat slower; i.e., at 67.4% conversion, 60.8% *trans*-propenylbenzene was observed.

The mechanistic aspects of this catalytic reaction, along with the olefin hydrogenation reaction, are presently under careful scrutiny. Preliminary observations are consistent with what is known about the analogous sulfonated phosphine systems.[12,14] Although the catalytic activities of the ruthenium sulfonated-phosphine complexes are higher by a factor of 30 than those for the PTA derivatives reported herein, solutions of $RuCl_2(PTA)_4$ are much more stable in air. Hence, it is apparent from these preliminary studies that the water-soluble, air-stable phosphine 1,3,5-triaza-7-phosphaadamantane is an attractive alternative to sulfonated phosphines for purposes of organometallic catalysis in aqueous or biphasic solutions. Furthermore, the PTA ligand is not a pronounced surfactant, as are the sulfonated phosphines, thus providing better phase separations.

Acknowledgment. The financial support of this research by the National Science Foundation (Grants CHE88-17873 and INT90-08227) and Hungarian Academy of Sciences (30.008/134/90) is greatly appreciated. We are

---

(9) Similarly, the N–C distances in the nonprotonated derivative **2a** average 1.467 [8] Å.

(10) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Interscience: New York, 1988; Chapter 19. (b) A Rh(II) species, *trans*-$(PPh_3)_2RhCl_2$, has been structurally characterized: Ogle, C. A.; Masterman, T. C.; Hubbard, J. L. *J. Chem. Soc., Chem. Commun.* **1990**, 1733.

(11) Joo, F.; Benyei, A. *J. Organomet. Chem.* **1989**, *363*, C19.

(12) Benyei, A.; Joo, F. *J. Mol. Catal.* **1990**, *58*, 151.

(13) Using a 0.1 M HCl aqueous solution completely inhibited the hydrogenation of aldehydes with **2a** and greatly retarded that of allylbenzene by **4a**. ^{31}P NMR spectra of solutions of **2a** in the presence of increasing amounts of DCl indicated formation of $[RuCl_3(PTA)_2(D\text{-}PTA)]$ (**2c**), which is analogous to **4b** (vide infra), along with other higher "protonated" species.

(14) Grosselin, J. M.; Mercier, C.; Allmang, G.; Grass, F. *Organometallics* **1991**, *10*, 2126.

especially grateful to Dr. Donald J. Daigle of the USDA Southern Regional Research Center (New Orleans, LA) for the generous sample of 1. The assistance of Matthew Holtcamp and Nicole White is gratefully acknowledged.

Supplementary Material Available: Tables giving details of catalyzed hydrogenation processes using **4a** as catalyst, an ORTEP drawing of **2b**, and X-ray crystallographic tables for compounds **2a**, **2b**, and **4b**, including the atomic coordinates, anisotropic thermal parameters, bond angles, and bond distances (14 pages). Ordering information is given on any current masthead page.

OM910751X

Bimetallic Iron Complexes with Carboxyethylene Bridges

Dorothy H. Gibson,* Jaime O. Franco, Michael T. Harris, and Tek-Sing Ong

Department of Chemistry, University of Louisville, Louisville, Kentucky 40292

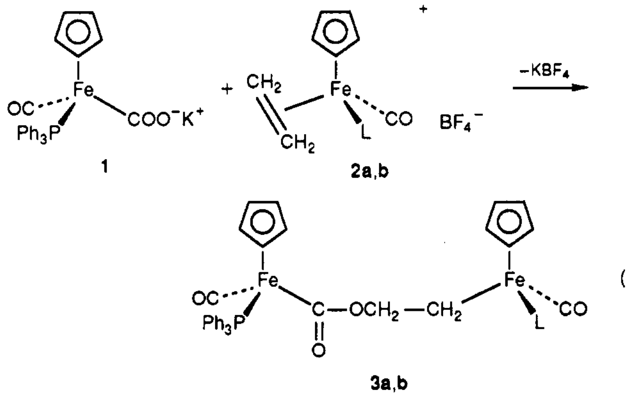
Received March 3, 1992

Summary: Reactions of the iron metallocarboxylate anion $CpFe(CO)(PPh_3)COO^-K^+$ (**1**) with ethylene-coordinated cations $CpFe(CO)(L)(C_2H_4)^+BF_4^-$ ($L = PPh_3$, $P(OPh)_3$) yield bimetallic complexes with a carboxyethylene bridge (**3a,b**); a pair of diastereomers, formed in nearly equal amounts, is produced in each case. Reactions of the bimetallic compounds with excess HBF_4 yield $CpFe(CO)_2(PPh_3)^+BF_4^-$ and $CpFe(CO)(L)(C_2H_4)^+BF_4^-$. Methanolysis of the carboxyethylene complexes yields $CpFe(CO)(PPh_3)COOCH_3$ and $CpFe(CO)(L)CH_2CH_2OCH_3$ (**7a,b**). Solvolysis of the latter compounds in ethanol gives the corresponding ethoxyethyl complexes **8a,b**. All new compounds have been fully characterized.

One of the ways being sought to utilize CO_2 as a building block for organic compounds involves its catalytic combination with alkenes, including ethylene. Several model stoichiometric reactions have been reported in which metal-bound ethylene has combined with CO_2 to generate new compounds, usually metallacycles;[1] in each product, the newly added carboxylate group is bound through oxygen to a transition-metal center. Also, bimetallic complexes with two acrylate bridging groups have been formed by insertion of CO_2 into carbon–hydrogen bonds in coordinated ethylene ligands.[2] Both catalytic and stoichiometric reactions have been initiated through C–C bond formation; new C–O bonds resulted from subsequent chemical degradations and afforded carboxylic acids or their derivatives (e.g., esters and lactones). The oxophilicity of the metal center does not seem to be critical, since early and late transition metals yield the same types of products. It has been often assumed that binding of CO_2 to the metal center precedes the reaction with a coordinated ethylene (or diene) ligand, but tangible evidence for this assumption is sparse.[3]

As noted previously, the binding of an alkene to a transition metal renders the alkene more susceptible to nucleophilic attack, particularly when the metal complex is cationic.[4] The increased reactivity has been attributed to "slippage" of the alkene to resemble an η^1 complex. Examples of the addition of nitrogen, phosphorus, and oxygen nucleophiles, as well as some carbon nucleophiles, are known.

We have examined the behavior of the carbon dioxide complex $CpFe(CO)(PPh_3)COO^-K^+$ (1)[5] toward ethylene-coordinated cations to determine whether the CO_2 ligand would be activated toward a metal-bound alkene. Our previous work with compound 1 demonstrated its weakly nucleophilic characteristics through its reactions with strong alkylating agents and with triphenyltin chloride.[5] With the two ethylene complexes[6] we have studied thus far, reactions with 1 lead to bimetallic complexes with bridging carboxyethylene groups:



(1)

a, L = PPh$_3$; b, L = P(OPh)$_3$

The compounds are obtained in very good yields (75–83%) as a pair of diastereomers (nearly equal amounts) in each case; separation of the isomers has not yet been accomplished. To our knowledge, this type of coupling of CO_2 to ethylene has not been observed before. The new compounds provide models for catalytic intermediates in

---

(1) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747.

(2) Alvarez, R.; Carmona, E.; Galindo, A.; Gutierrez, E.; Marin, J. M.; Monge, A.; Poveda, M. L.; Ruiz, C.; Savariault, J. M. *Organometallics* **1989**, *8*, 2430.

(3) Braunstein, P.; Matt, D.; Nobel, D. *J. Am. Chem. Soc.* **1988**, *110*, 3207.

(4) (a) Busetto, L.; Palazzi, A.; Ros, R.; Belluco, U. *J. Organomet. Chem.* **1970**, *25*, 207. (b) Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122. (c) Reger, D. L. *Inorg. Chem.* **1975**, *14*, 660. (d) Knoth, W. H. *Inorg. Chem.* **1975**, *14*, 4566. (e) Lennon, P.; Rosan, A. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 8426. (f) Kegley, S. E.; Bergstrom, D. T.; Crocker, L. S.; Weiss, E. P.; Berndt, W. G.; Rheingold, A. L. *Organometallics* **1991**, *10*, 567. (g) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308. (h) Chang, T. C. T.; Foxman, B. M.; Rosenblum, M.; Stockman, C. *J. Am. Chem. Soc.* **1981**, *103*, 7361.

(5) Gibson, D. H.; Ong, T.-S.; Ye, M. *Organometallics* **1991**, *10*, 1811.

(6) (a) Compound **2a**: Davison, A.; Reger, D. L. *J. Am. Chem. Soc.* **1972**, *94*, 9237. (b) Compound **2b**: Reger, D. L.; Coleman, C. J. *Inorg. Chem.* **1979**, *18*, 3155.

0276-7333/92/2311-1993$03.00/0