Reversible Arm-Off Dissociation of the Tripodal $MeC(CH_2PPh_2)_3$ in $HRh(CO)[MeC(CH_2PPh_2)_3]$ under Hydroformylation Conditions

Gábor Kiss[†] and István T. Horváth*

Corporate Research Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801

Received August 8, 1991

Summary: The reversible arm-off dissociation of the tripodal ligand $MeC(CH_2PPh_2)_3$ in $HRh(CO)[\eta^3\text{-}MeC(CH_2PPh_2)_3]$ (**1**) under H_2/CO (1:1) was studied by high-pressure IR and NMR spectroscopy. The formation of $HRh(CO)_2[\eta^2\text{-}MeC(CH_2PPh_2)_3]$ (**2**) was observed, which explains the low *n*/*i* ratio observed for the hydroformylation of olefins.

The application of tripodal phosphine ligands in homogeneous catalysis has received considerable interest.[1] While η^3-coordinated tripodal ligands provide a rigid geometry around the metal center, dissociation of a phosphine arm results in η^2-coordination of higher flexibility. This process, known as "arm-off" dissociation, has been implicated in several organometallic and catalytic reactions involving tripodal phosphine ligands.[2] Venanzi and co-workers have postulated that the formation of $HRh(CO)[\eta^3\text{-}MeC(CH_2PPh_2)_3]$ (1) from $H_3Rh[\eta^3\text{-}MeC(CH_2PPh_2)_3]$ and CO involves the initial dissociation of one of the phosphine arms of $MeC(CH_2PPh_2)_3$ to generate a coordinatively unsaturated intermediate, $H_3Rh[\eta^2\text{-}MeC(CH_2PPh_2)_3]$.[2d] Caulton and co-workers have recently reported evidence for the formation of $MeCORh(CO)_2[\eta^2\text{-}MeC(CH_2PPh_2)_3]$.[2g] The formation of a rhodium complex containing $P(CH_2CH_2PPh_2)_3$ with a free phosphine arm was also detected by Bianchini et al.[2f] We now wish to present the first experimental evidence for the reversible dissociation of a phosphine arm of $MeC(CH_2PPh_2)_3$ in 1 under hydroformylation conditions, resulting in $HRh(CO)_2[\eta^2\text{-}MeC(CH_2PPh_2)_3]$ (2).

$HRh(CO)[\eta^3\text{-}MeC(CH_2PPh_2)_3]$ (1) was prepared by the reaction of equimolar $Rh(CO)_2(acac)$ and $MeC(CH_2PPh_2)_3$ under H_2/CO (1:1) in THF.[3] The reversible reaction of 1 with CO under H_2/CO was studied by high-pressure IR[4] and NMR[5] spectroscopy. The IR spectrum of a yellow solution of 1 in THF (8 mmol/L) shows to bands at 1940 (vw) and 1909 (vs) cm^{-1}, which are due to the H-Rh and terminal carbonyl vibrations (Figure 1). When the solution was treated with H_2/CO up to 1100 psi, the intensities of these bands decreased and two new bands appeared at 1989 (s) and 1943 (vs) cm^{-1}. Since the same bands were also observed by performing the reaction with $DRh(CO)[\eta^3\text{-}MeC(CH_2PPh_2)_3]$ under D_2/CO, they are attributed to terminal carbonyl vibrations. The ratio between the intensities of the new bands does not change by changing the H_2/CO pressure, indicating that only one new compound is formed. The concentration of 1 decreased linearly by increasing the CO pressure. Finally, when the pressure was decreased to 15 psi, 1 re-formed quantitatively. These results suggested the facile formation of

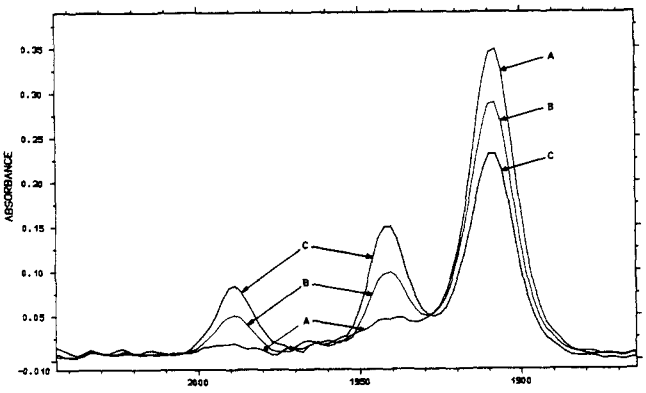


Figure 1. High-pressure IR spectra of $HRh(CO)[\eta^3\text{-}MeC(CH_2PPh_2)_3]$ (1) in THF under 90 (A), 600 (B), and 1100 (C) psi of H_2/CO pressure at room temperature.

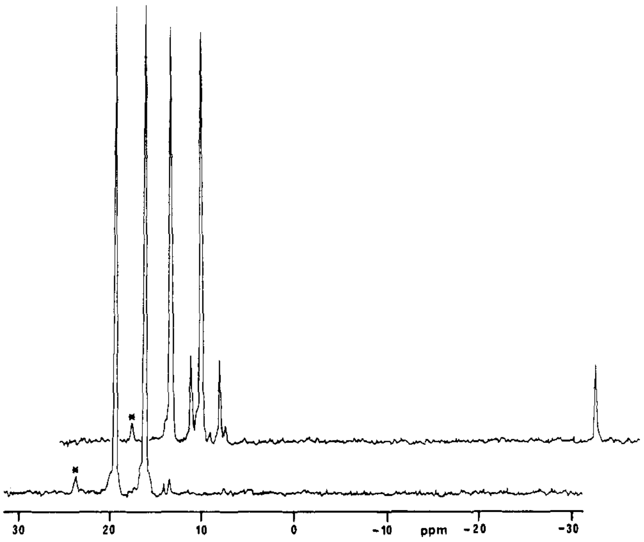
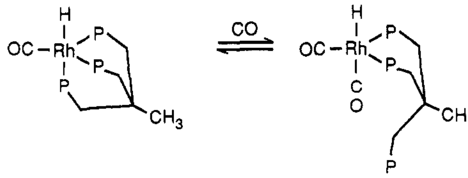


Figure 2. High-pressure ^{31}P NMR spectra of $HRh(CO)[\eta^3\text{-}MeC(CH_2PPh_2)_3]$ (1) in THF-d_8 under 15 and 450 psi of H_2/CO pressure at room temperature. The small peaks labeled with asterisks are due to phosphine oxide impurities.

Scheme I



[†] Summer intern from the University of Miami, Coral Gables, FL.

(1) Meek, D. W. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983.

(2) (a) Chatt, J.; Hart, F. A.; Watson, H. R. *J. Chem. Soc.* **1962**, 2537. (b) Siegel, W. O.; Lapporte, S. J.; Collman, J. P. *Inorg. Chem.* **1971**, *10*, 2158. (c) DuBois, D. L.; Meek, D. W. *Inorg. Chim. Acta* **1976**, *19*, L29. (d) Ott, J.; Venanzi, L. M.; Ghilardi, C. A.; Midollini, S.; Orlandini, A. *J. Organomet. Chem.* **1985**, *291*, 89. (e) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Fujiwara, Y.; Jintoku, T.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1988**, 299. (f) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 6411. (g) Thaler, E. G.; Folting, K.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 2664. (h) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Ramirez, J. A. *Organometallics* **1990**, *9*, 226. (i) Rauscher, D. J.; Thaler, E. G.; Huffman, J. C.; Caulton, K. G. *Organometallics* **1991**, *10*, 2209.

(3) A solution of 1.6 mmol of $Rh(CO)_2(acac)$ and 1.6 mmol of $MeC(CH_2PPh_2)_3$ in 200 mL of THF was treated with 450 psi of H_2/CO (1:1) for 30 min.[4] The pressure was decreased to 15 psi, and the solution was transferred into a Schlenk tube under N_2. The product $HRh(CO)[\eta^3\text{-}MeC(CH_2PPh_2)_3]$ (1) was isolated in 99.5% yield.

(4) The reaction was performed in a 300-mL stainless steel autoclave connected to a Tempco high-pressure IR cell.

(5) Horváth, I. T.; Ponce, E. C. *Rev. Sci. Instrum.* **1991**, *62*, 1104.

0276-7333/91/2310-3798$02.50/0

$HRh(CO)_2[\eta^2\text{-}MeC(CH_2PPh_2)_3]$ (2), containing a free phosphine arm (Scheme I).

The exact coordination mode of the triphos ligand in 2 was established by high-pressure NMR spectroscopy. The ^{31}P NMR spectrum of 1 (0.05 mmol) in 1.8 g of THF-d_8 shows a doublet at 18 ppm (J_{Rh-P} = 118 Hz; Figure 2), indicating three chemically equivalent $-CH_2PPh_2$ arms bonded to rhodium.[2d] When the solution was charged with 450 psi of H_2/CO (1:1), the intensity of the doublet decreased and two new resonances appeared (Figure 2), a doublet at 15.9 ppm (J_{Rh-P} = 113 Hz) and a singlet at −26.8 ppm, with relative intensities of 2:1, respectively. These resonances are assigned to an $\eta^2\text{-}MeC(CH_2PPh_2)_3$ ligand in 2, which has one $-CH_2PPh_2$ arm not bonded to the rhodium. When the pressure was increased to 900 psi, the relative intensity of the doublet at 18.0 ppm further decreased and the intensity of the resonance assigned to $\eta^2\text{-}MeC(CH_2PPh_2)_3$ proportionally increased. Measurements of the equilibrium between 1 and 2 are in progress.

In conclusion, we have established by high-pressure IR and NMR spectroscopy that the tripodal ligand $MeC(CH_2PPh_2)_3$ can readily undergo reversible dissociation of one of its phosphine arms under hydroformylation conditions. The arm-off dissociation can rationalize the low *n*/*i* selectivities frequently observed in the catalytic hydroformylation of olefins using triphos-modified rhodium catalysts.[2e,6] The coordination of the $\eta^2\text{-}MeC(CH_2PPh_2)_3$ ligand to rhodium is similar to that of $\eta^2\text{-}Ph_2P(CH_2)_3PPh_2$, and bis(diphenylphosphino)alkane-modified rhodium hydroformylation catalysts are known to give low *n*/*i* ratios.[7]

Acknowledgment. The very careful technical work by Raymond A. Cook is gratefully acknowledged.

---

(6) Our results on the hydroformylation of hexene-1 at 100 °C and 450 psi of H_2/CO pressure using 1 as catalyst were very similar to those reported by Bianchini and co-workers.[2e]

(7) (a) Sanger, A. R. *J. Mol. Catal.* **1977**, *3*, 221. (b) Pittman, C. V.; Hiraio, A. *J. Org. Chem.* **1978**, *43*, 640.

Approaches to Hexane-Soluble Cationic Organometallic Lewis Acids. Synthesis, Structure, and Solubility of Titanium Complexes of the Formula $[(\eta^5\text{-}C_5(Si(CH_3)_3)_nH_{5-n})Ti(acac)_2]^+OTf^-$ (*n* = 2, 3)

Charles H. Winter,* Xiao-Xing Zhou,[1] and Mary Jane Heeg
Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received July 15, 1991

Summary: Treatment of (1,3-bis(trimethylsilyl)cyclopentadienyl)titanium trichloride with silver triflate (1 equiv) and acetylacetone $RCOCH_2COR$ (2 equiv, R = CH_3, ^{t}Bu, CF_3) in dichloromethane affords the triflate complexes $[(1,3\text{-}C_5(Si(CH_3)_3)_2H_3)Ti(CH_3COCHCOCH_3)_2]^+TfO^-$, $[(1,3\text{-}C_5(Si(CH_3)_3)_2H_3)Ti(^tBuCOCHCO^tBu)_2]^+TfO^-$, and $[(1,3\text{-}C_5(Si(CH_3)_3)_2H_3)Ti(CF_3COCHCOCF_3)_2OTf]$. Similar reactions using (1,2,4-tris(trimethylsilyl)cyclopentadienyl)titanium trichloride and $RCOCH_2COR$ (R = ^{t}Bu, CF_3) give $[(1,2,4\text{-}C_5(Si(CH_3)_3)_3H_2)Ti(^tBuCOCHCO^tBu)_2]^+TfO^-$ and $[(1,2,4\text{-}C_5(Si(CH_3)_3)_3H_2)Ti(CF_3COCHCOCF_3)_2OTf]$. These complexes exhibit modest to excellent solubility in alkane and perfluoroalkane solvents and demonstate that ionic complexes can be solubilized into even the most nonpolar solvents with the appropriate choice of ligands. The ionic versus molecular nature of the complexes has been established through crystal structure determinations for $[(1,3\text{-}C_5(Si(CH_3)_3)_2H_3)Ti(CH_3COCHCOCH_3)_2]^+TfO^-$ and $[(1,3\text{-}C_5(Si(CH_3)_3)_2H_3)Ti(CF_3COCHCOCF_3)_2OTf]$.

Cationic transition-metal complexes possessing an available coordination site promote a number of important reactions, including olefin polymerizations,[2] alkene and alkyne hydrogenations,[3] and many others.[4] The high reactivity associated with these complexes arises at least in part from the enhanced electrophilicity of the metal center, which favors strong coordination of the organic fragments. However, the extreme Lewis acidity of the cationic site can lead to variety of deactivation processes, including atom abstraction from a reactive solvent[5] and strong coordination of the solvent required to solubilize an ionic complex.[6] For these reasons, it would often be desirable to conduct catalytic transformations in solvents of low nucleophilicity and reactivity, such as saturated alkanes or perfluoroalkanes. Unfortunately, cationic transition-metal complexes tend to be rigorously insoluble in such media. We have therefore sought to develop ligands for cationic complexes that boost solubility in nonpolar solvents without kinetically deactivating the resultant species.[7] In this context, we report the synthesis, structure, and solubility of complexes of the formula $[(\eta^5\text{-}C_5(Si(CH_3)_3)_nH_{5-n})Ti(acac)_2]^+OTf^-$ (*n* = 2, 3; acac = CH_3, CF_3, and ^{t}Bu 2,4-disubstituted acetylacetonates). These complexes exhibit modest to excellent solubility in alkane and perfluoroalkane solvents and demonstrate that ionic complexes can be solubilized into even the most nonpolar solvents with the appropriate choice of ligands.

---

(1) Wilfrid Heller Fellow, 1991–1992.

(2) For selected examples, see: Bochmann, M.; Jagger, A. J.; Nicholls, J. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 780. Brookhart, M.; Lincoln, D. M.; Volpe, A. F., Jr.; Schmidt, G. F. *Organometallics* **1989**, *8*, 1212. Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892. Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. Tabue, R.; Krukowwa, L. *J. Organomet. Chem.* **1988**, *347*, C9. Gassman, P. G.; Callstrom, M. R. *J. Am. Chem. Soc.* **1987**, *109*, 7875. Jordan, R. F.; Echols, S. F. *Inorg. Chem.* **1987**, *26*, 383. Bochmann, M.; Wilson, L. M. *J. Chem. Soc., Chem. Commun.* **1986**, 1610. Eisch, J. J.; Piotrowski, A. M.; Brownstein, S. K.; Gabe, E. R.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 7219.

(3) For leading references, see: Halpern, J. *Science* **1982**, *217*, 401. Crabtree, R. *Acc. Chem. Res.* **1979**, *12*, 331.

(4) For leading references, see: Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405.

(5) Jordan, R. F.; LaPointe, R. E.; Bajgur, C. S.; Echols, S. F.; Willett, R. *J. Am. Chem. Soc.* **1987**, *109*, 4111.

(6) For examples of solvent coordination by cationic organometallic Lewis acids, see: Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89. Colsman, M. R.; Newbound, T. D.; Marshall, L. J.; Noirot, M. D.; Miller, M. M.; Wulfsberg, G. P.; Frye, J. S.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 2349. Fernandez, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207. Boyle, P. F.; Nicholas, K. M. *J. Organomet. Chem.* **1976**, *114*, 307. Ferguson, J. A.; Meyer, T. J. *Inorg. Chem.* **1971**, *10*, 1025.

(7) (a) Winter, C. H.; Kampf, J. W.; Zhou, X.-X. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1990**, *C46*, 1231. (b) Winter, C. H.; Zhou, X.-X.; Dobbs, D. A.; Heeg, M. J. *Organometallics* **1991**, *10*, 210. (c) Winter, C. H.; Dobbs, D. A.; Zhou, X.-X. *J. Organomet. Chem.* **1991**, *403*, 145.

0276-7333/91/2310-3799$02.50/0