justified by the existing data on this system. In summary, this is the first direct evidence of ISC from the S_2 state.

Acknowledgment. The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy, USA and the Department of Science and Technology, Government of India (Grant No. SR/OY/C07/90). This is document No. NDRL-3346 from the Notre Dame Radiation Laboratory. The author thanks Prof. R. W. Fessenden for his association with the earlier works on this system and to Prof. M. Chowdhury and Dr. M. Durgaprasad for their valuable suggestions.

Registry No. Acenaphthylene, 208-96-8.

Rapid Intermolecular Ligand Exchange between Square-Planar Iridium(I) Complexes: *trans*-$Ir(CO)L_2X$ ($X = Cl$ or Me, $L = P(p\text{-tolyl})_3$ or $PMePh_2$)

Jeffrey S. Thompson and Jim D. Atwood*

Department of Chemistry, University at Buffalo
State University of New York, Buffalo, New York 14214

Received April 22, 1991

Square-planar complexes provide one of the foundations of inorganic and organometallic chemistry.[1] Reactivity studies of square-planar complexes have centered on substitution[1] and oxidative addition reactions.[1,2] In the course of our studies of iridium(I) complexes,[3] we have discovered an extremely facile ligand-exchange process for the complexes *trans*-$Ir(CO)L_2X$ ($L = P(p\text{-tolyl})_3$ and $PMePh_2$, $X = Cl$, Me, or OMe).

The compounds *trans*-$Ir(CO)(P(p\text{-tolyl})_3)_2X$, $X = Cl$, Me, and OMe, have been previously reported.[3,4] The characterizations are consistent with those previously reported.[4] *trans*-$Ir(CO)(Cl)(PMePh_2)_2$ was prepared by ligand exchange on *trans*-$Ir(CO)(Cl)(PPh_3)_2$.[5] The methyl complex *trans*-$Ir(CO)(Me)(PMePh_2)_2$ was prepared from the chloride by the same procedure as for *trans*-$Ir(CO)(Me)(P(p\text{-tolyl})_3)_2$.[6] The main technique used in this study is ^{31}P NMR spectroscopy; Table I contains the ^{31}P resonances of the complexes and free ligands.

Table I. ^{31}P NMR Resonances in CD_2Cl_2 for Various Complexes

reagents	^{31}P NMR, ppm
$Ir(CO)(Cl)(P(p\text{-tolyl})_3)_2$	22.5 (s)
$Ir(CO)Me(P(p\text{-tolyl})_3)_2$	28.2 (s)
$Ir(CO)(Cl)(PMePh_2)_2$	9.4 (s)
$Ir(CO)Me(PMePh_2)_2$	10.2 (s)
$PMePh_2$	−26.85 (s)
$P(p\text{-tolyl})_3$	−7.96 (s)

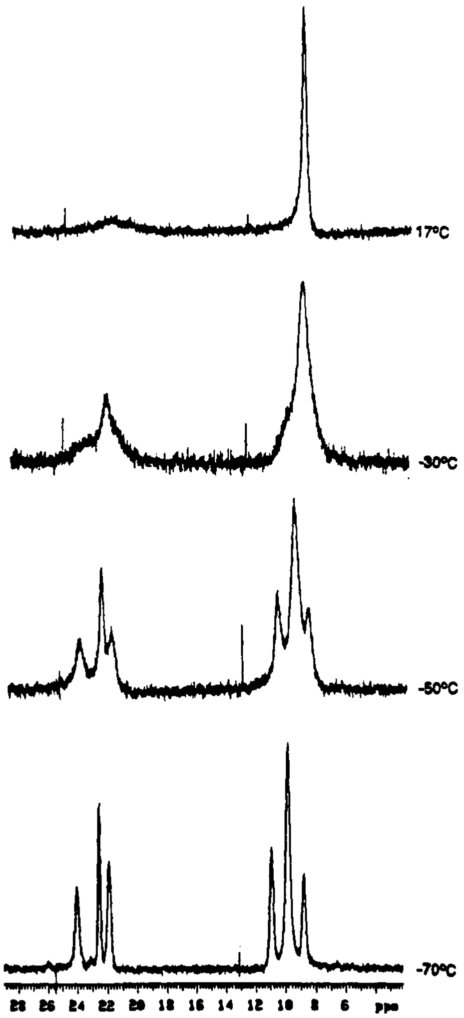

Figure 1. ^{31}P NMR spectra recorded at four temperatures for a mixture of *trans*-$Ir(CO)(Cl)(P(p\text{-tolyl})_3)_2$ (22.4 (s) ppm) and *trans*-$Ir(CO)(Cl)(PMePh_2)_2$ (10.0 (s) ppm). Even at −70 °C, these are fully exchanged with formation of *trans*-$Ir(CO)(Cl)(P(p\text{-tolyl})_3)(PMePh_2)$ (2 d, 23 and 10 ppm). As the temperature is warmed, the exchange becomes rapid.

In a typical reaction (represented for the methyl compounds), 25 mg of *trans*-$Ir(CO)(Me)(P(p\text{-tolyl})_3)_2$ and 25 mg of *trans*-$Ir(CO)(Me)(PMePh_2)_2$ were placed in an NMR tube equipped with a vacuum adaptor, which was then removed from the inert-atmosphere glovebox and placed on a high-vacuum line. The solids were evacuated and cooled to $N_2(l)$ temperature, and 1.0 mL of CD_2Cl_2 was added by vacuum distillation. The sample was placed frozen in the NMR instrument (Varian VXR-400) and monitored from −70 °C to room temperature by ^{31}P NMR spectroscopy. Figure 1 shows spectra for a typical reaction. Proton spectra were also recorded but were quite complicated, and we did not attempt assignment.

For each reaction of *trans*-$Ir(CO)(P(p\text{-tolyl})_3)_2X$ with *trans*-$Ir(CO)(PMePh_2)_2X$, three species are present in approximately statistical amounts at −70 °C: *trans*-$Ir(CO)(P(p\text{-tolyl})_3)_2X$, *trans*-$Ir(CO)(PMePh_2)_2X$, and *trans*-$Ir(CO)(PMePh_2)(P(p\text{-tolyl})_3)X$.[7] The mixed phosphine complex shows two doublets with coupling ($J_{P-P} \cong 300$ Hz) typical for trans phosphines.[8]

---

[1] (a) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; John Wiley: New York, 1968. (b) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, CA, 1985.

[2] (a) Collman, J. P.; Roper, W. R. *Adv. Organomet. Chem.* **1968**, *7*, 53. (b) Halpern, J. *Acc. Chem. Res.* **1970**, *3*, 386. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

[3] (a) Thompson, J. S.; Bernard, K. A.; Rappoli, B. J.; Atwood, J. D. *Organometallics* **1990**, *9*, 2727. (b) Rappoli, B. J.; McFarland, J. M.; Thompson, J. S.; Atwood, J. D. *J. Coord. Chem.* **1990**, *21*, 147. (c) Bernard, K. A.; Atwood, J. D. *Organometallics* **1989**, *8*, 795. (d) Rees, W.; Churchill, M. R.; Li, Y. G.; Atwood, J. D. *Organometallics* **1985**, *4*, 1162. (e) Thompson, J. S.; Atwood, J. D. *Organometallics*. In press.

[4] (a) Rappoli, B. J.; Janik, T. S.; Churchill, M. R.; Thompson, J. S.; Atwood, J. D. *Organometallics* **1988**, *7*, 1939. (b) Rees, W. M.; Churchill, M. R.; Rappoli, B. J.; Janik, T. S.; Atwood, J. D. *J. Am. Chem. Soc.* **1987**, *109*, 5145.

[5] Collman, J. P.; Kang, J. W. *J. Am. Chem. Soc.* **1967**, *89*, 844.

[6] *trans*-$Ir(CO)(Cl)(PMePh_2)_2$: IR (KBr) $\nu_{CO} = 1950\ cm^{-1}$; ^{31}P NMR 9.5 (s) ppm. *trans*-$Ir(CO)(Me)(PMePh_2)_2$: IR (KBr) $\nu_{CO} = 1925\ cm^{-1}$; ^{31}P NMR (C_6D_6) 10.6 (s) ppm; ^1H NMR (C_6D_6) 0.42 (t), $J_{P-H} = 9.5$ Hz, 2.0 (s), 2.3 (t), $J_{P-H} = 3.2$ Hz, 6.9 (m), 7.6 (m).

[7] Integration of the −70 °C ^{31}P NMR spectrum for reaction of *trans*-$Ir(CO)(Cl)(P(p\text{-tolyl})_3)_2$ with *trans*-$Ir(CO)(Cl)(PMePh_2)_2$ in a 1:2 ratio results in a 1:3:4 ratio of *trans*-$Ir(CO)(Cl)(P(p\text{-tolyl})_3)_2$, *trans*-$Ir(CO)(Cl)(PMePh_2)$, and *trans*-$Ir(CO)(Cl)(P(p\text{-tolyl})_3)(PMePh_2)$.

0002-7863/91/1513-7429$02.50/0

Thus, even at −70 °C, the phosphines are fully exchanged. As the temperature is increased, the rate of exchange becomes competitive on the NMR time scale and broadened resonances are observed.

$$\textit{trans}\text{-Ir(CO)(P(}p\text{-tolyl)}_3)_2\text{X} + \textit{trans}\text{-Ir(CO)(PMePh}_2)_2\text{X} \rightleftarrows 2\,\textit{trans}\text{-Ir(CO)(P(}p\text{-tolyl)}_3\text{(PMePh}_2)\text{X}$$

Very similar exchanges are observed between complexes with different X groups. Reaction between *trans*-Ir(CO)(Me)(P(*p*-tolyl)$_3$)$_2$ and *trans*-Ir(CO)(Cl)(PMePh$_2$)$_2$ results in a statistical mixture of *trans*-Ir(CO)(Cl)(PMePh$_2$)$_2$, trans-Ir(CO)(Me)(PMePh$_2$)$_2$, *trans*-Ir(CO)(Cl)(P(*p*-tolyl)$_3$)$_2$, *trans*-Ir(CO)(Me)(P(*p*-tolyl)$_3$)$_2$, *trans*-Ir(CO)(Cl)(PMePh$_2$)(P(*p*-tolyl)$_3$), and *trans*-Ir(CO)(Me)(PMePh$_2$)(P(*p*-tolyl)$_3$) at −70 °C. In this reaction the spectra remain sharp at room temperature. Reaction of *trans*-Ir(CO)(OMe)(P(*p*-tolyl)$_3$)$_2$ with *trans*-Ir(CO)(Cl)(PMePh$_2$)$_2$ also leads to the full range of exchanged products. In this reaction, by −30 °C all of the resonances broaden.

The reactions described above show a surprisingly facile intermolecular exchange process. Formation of the mixed phosphine product requires that the phosphine is the group transferred. Square-planar complexes are known to undergo facile associative substitution.[1] Although a phosphine bridging two metals is not common, an association with bridging X groups leading to phosphine exchange would be possible. However, a dependence on the bridging group X might be expected. For X = Me, OMe, or Cl, the exchange has been completed by −70 °C. An alternate possibility would be phosphine dissociation from a square-planar complex producing Ir(CO)LX and L.[9–11] The L could then exchange with other iridium complexes leading to effective L transfer. Dissociation of PPh$_3$ from Rh(Cl)(PPh$_3$)$_3$ was shown to occur with a rate constant of 0.71 s^{-1},[10] although the equilibrium constant for PPh$_3$ dissociation is $\sim 10^{-7}$ M.[9] A very small equilibrium constant would be consistent with our inability to observe free L in our reactions. Other examples of phosphine dissociation from square-planar complexes have not been reported. When excess PMePh$_2$ is added to *trans*-Ir(CO)(Cl)(P(*p*-tolyl)$_3$)$_2$ at −70 °C, the spectrum is invariant as one warms the sample to room temperature, with free P(tolyl)$_3$ and a broad resonance at −16.2 ppm that is probably due to the five-coordinate complex Ir(CO)(Cl)(PMePh$_2$)$_3$. The same species is formed by addition of PMePh$_2$ to *trans*-Ir(CO)(Cl)(PMePh$_2$)$_2$. Addition of P(*p*-tolyl)$_3$ to *trans*-Ir(CO)(Cl)(P(*p*-tolyl)$_3$)$_2$ at a 0.1 molar ratio shows ^{31}P resonances for free P(*p*-tolyl)$_3$ and *trans*-Ir(CO)(Cl)(P(*p*-tolyl)$_3$)$_2$ at −70 °C, but both are broadened significantly.

We cannot completely exclude exchange caused by reaction of the square-planar complexes with traces of free phosphine. The samples used are recrystallized, show no trace of free phosphine in the ^{31}P spectrum, and show no time- or temperature-dependent NMR spectra. Thus it is unlikely that free phosphine is responsible for these reactions.

On the basis of the similarity in the rates to those observed for addition of free phosphine and the known phosphine dissociation from Rh(Cl)(PPh$_3$)$_3$, it is probable that the rapid phosphine exchange observed between square-planar iridium complexes occurs through dissociation of phosphine from an iridium and subsequent associative reactions of the free phosphine with square-planar complexes.

Acknowledgment. We are grateful for support from the National Science Foundation (CHE-9015897) for this research. The Varian VXR-400 NMR instrument was purchased through a grant from the Department of Education (2-2-01011).

---

(8) *trans*-Ir(CO)(Cl)(PMePh$_2$)(P(*p*-tolyl)$_3$): ^{31}P NMR 10.1 (d), 29.0 (d), $J_{\text{P-P}} = 300$ Hz. *trans*-Ir(CO)(Me)(PMePh$_2$)(P(*p*-tolyl)$_3$): ^{31}P NMR 9.9 (d), 23.0 (d), $J_{\text{P-P}} = 340$ Hz. *trans*-Ir(CO)(OMe)(PMePh$_2$)(P(*p*-tolyl)$_3$): ^{31}P NMR 9.8 (d), 25.6 (d), $J_{\text{P-P}} = 370$ Hz.

(9) Wink, D. A.; Ford, P. C. *J. Am. Chem. Soc.* **1987**, *109*, 436.

(10) Halpern, J. A.; Wong, C. S. *J. Chem. Soc., Chem. Commun.* **1973**, 629.

(11) (a) Faraone, G.; Ricevuto, V.; Romeo, R.; Trozzi, M. *J. Chem. Soc. A* **1971**, 1877. (b) Romeo, R. *Comments Inorg. Chem.* **1990**, *11*, 21.

Solvent Effects on a Diels–Alder Reaction from Computer Simulations

James F. Blake and William L. Jorgensen*

Department of Chemistry, Yale University
New Haven, Connecticut 06511-8118

Received June 3, 1991

The traditional notion that the rates of Diels–Alder reactions are insensitive to solvent effects[1] is certainly false in aqueous media.[2–6] For example, rate accelerations of 741 and 6805 have been obtained in water for the reactions of cyclopentadiene (CP) with methyl vinyl ketone (MVK)[2a] and a quinone.[6] Suggested origins of the effects are hydrophobic association,[2,4,6] micellar catalysis,[3a,b] high internal solvent pressure,[3c] solvent polarity,[5] and hydrogen bonding.[7] In order to probe this phenomenon further, we have carried out Monte Carlo simulations to compute the changes in free energy of solvation (ΔG_{sol}) during the reaction of CP and MVK in liquid propane, methanol, and water.

The approach is an updated version of our efforts on S$_\text{N}$2, addition, and association reactions.[8] To begin, ab initio molecular orbital calculations were used to determine the minimum energy reaction path (MERP) in the gas phase. Houk and co-workers previously found only minor variations in transition-state (TS) structure for the reaction of 1,3-butadiene and acrolein when optimized at the 3-21G, 6-31G(d), and MP2/6-31G(d) levels.[9] Accordingly, we located the four transition states for CP plus MVK corresponding to MVK being s-cis or s-trans and the approach being exo or endo with the 3-21G basis set, and 6-31G(d)//3-21G calculations were subsequently performed.[10] Consistent with the acrolein precedent,[9] the endo-cis TS was found to be lowest in energy. This TS provided a starting point for the reaction path following procedure in GAUSSIAN 90 that traces the MERP from TS to reactants and product.[11,12] Essentially, a movie containing 65 frames was obtained covering reaction coordinate (r_c, defined as the average of the lengths of the two forming C–C bonds) values from 1.5 to 8.2 Å. Four frames are condensed in Figure 1.

The next issue is the intermolecular potential functions for the fluid simulations. Well-proven potentials for the solvents are available; the TIP4P model was adopted for water along with the OPLS potentials for propane and methanol.[13] The latter employ

---

(1) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.

(2) (a) Rideout, D. C.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 7816. (b) Breslow, R.; Maitra, U.; Rideout, D. *Tetrahedron Lett.* **1983**, *24*, 1901. (c) Breslow, R.; Maitra, U. *Tetrahedron Lett.* **1984**, *25*, 1239. (d) Breslow, R.; Guo, T. *J. Am. Chem. Soc.* **1988**, *110*, 5613. (e) Breslow, R.; Rizzo, C. J. *J. Am. Chem. Soc.* **1991**, *113*, 4340. (f) Breslow, R. *Acc. Chem. Res.* **1991**, *24*, 159.

(3) (a) Grieco, P. A.; Garner, P.; He, Z. *Tetrahedron Lett.* **1983**, *24*, 1897. (b) Grieco, P. A.; Yoshida, K.; Garner, P. *J. Org. Chem.* **1983**, *48*, 3137. (c) Grieco, P. A.; Nunes, J. J.; Gaul, M. D. *J. Am. Chem. Soc.* **1990**, *112*, 4595.

(4) (a) Schneider, H.-J.; Sangwan, N. K. *J. Chem. Soc., Chem. Commun.* **1986**, 1787. (b) Sangwan, N. K.; Schneider, H.-J. *J. Chem. Soc., Perkin Trans. 2*, **1989**, 1223.

(5) Cativiela, C.; Garcia, J. I.; Mayoral, J. A.; Avenoza, A.; Peregrina, J. M.; Roy, M. A. *J. Phys. Org. Chem.* **1991**, *4*, 48.

(6) Blokzijl, W.; Blandamer, M. J.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1991**, *113*, 4241.

(7) Rodgman, A.; Wright, G. F. *J. Org. Chem.* **1953**, *18*, 465. Kelly, T. R.; Meghani, P.; Ekkundi, V. S. *Tetrahedron Lett.* **1990**, *31*, 3381.

(8) For reviews, see: (a) Jorgensen, W. L. *Adv. Chem. Phys., Part II* **1988**, *70*, 469. (b) Jorgensen, W. L. *Acc. Chem. Res.* **1989**, *22*, 184.

(9) Birney, D. M.; Houk, K. N. *J. Am. Chem. Soc.* **1990**, *112*, 4127. Storer, J. W.; Raimondi, L.; Houk, K. N., to be published.

(10) The ab initio calculations were performed with GAUSSIAN 90, Revision F: Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A., Gauusian, Inc., Pittsburgh PA, 1990.

(11) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(12) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.

(13) (a) Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; Klein, M. L. *J. Chem. Phys.* **1983**, *79*, 926. (b) Jorgensen, W. L.; Madura, J. D.; Swenson, C. S. *J. Am. Chem. Soc.* **1984**, *106*, 6638. (c) Jorgensen, W. L. *J. Phys. Chem.* **1986**, *90*, 1276.

0002-7863/91/1513-7430$02.50/0