Synthesis and Reaction Chemistry of Water-Soluble *mer*-$(Me_3P)_3Ir(H)(H)Cl$: Activation by Water of Alkyne Insertion into an Ir–H Bond

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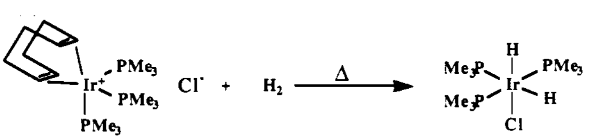
Summary: Reaction between $[Ir(COD)(PMe_3)_3]Cl$ *and* H_2 *leads to the formation of mer*-$(Me_3P)_3Ir(H)(H)Cl$ *in excellent yield. mer*-$(Me_3P)_3Ir(H)(H)Cl$ *is unreactive toward alkenes and alkynes in most organic solvents but is water-soluble and very reactive in aqueous solution. Reactions between mer*-$(Me_3P)_3Ir(H)(H)Cl$ *and alkynes are discussed, and the solid-state structure of a resulting vinyliridium hydride is described. mer*-$(Me_3P)_3Ir(H)(H)Cl$ *can be used as a homogeneous hydrogenation catalyst in water.*

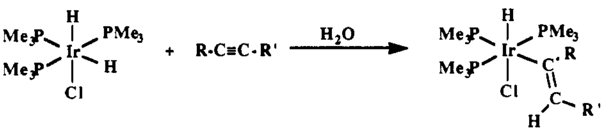
Over the last several years, there has been considerable interest in examining the chemistry of organometallic complexes in aqueous solution, with a particular focus on looking at homogeneous catalysis in water.[1] Most of this effort has involved taking systems that are typically not water-soluble and making them water-soluble via the functionalization of one or more of the ligands.[2] Even more intriguing are those complexes which are *intrinsically* water-soluble (solubility not dependent on a functionalized ligand) and whose organometallic chemistry is greatly influenced by the complex/water interaction.[3] This communication describes the synthesis and chemistry of a complex which fits into this latter category: *mer*-$(Me_3P)_3Ir(H)(H)(Cl)$.

Recently, we have reported on oxidative addition chemistry of $[Ir(COD)(PMe_3)_3]Cl$,[4] a convenient, stable source of "$Ir(PMe_3)_3Cl$". We have previously demonstrated the oxidative addition of B–H,[5] C–H,[6] N–H,[7] and O–H[8] bonds to this iridium(I) center. To add to these studies, we examined H–H addition and found that heating a slurry of $[Ir(COD)(PMe_3)_3]Cl$ in mesitylene to 80 °C under an atmosphere of dihydrogen leads to a nearly quantitative production of *mer*-$(Me_3P)_3Ir(H)(H)(Cl)$ (eq 1). *mer*-$(Me_3P)_3Ir(H)(H)(Cl)$ was characterized by a combination of NMR spectroscopies which clearly show the meridional arrangement of phosphines and the structure as depicted in eq 1.[9]



(1)

Our previous investigations into the reactivity of iridium hydride complexes formed from the oxidative addition of B–H, C–H, and N–H bonds showed a widely varying pattern of reactivity with respect to insertions of alkynes into the Ir–H bonds. In this study, *mer*-$(Me_3P)_3Ir(H)(H)(Cl)$ did not react directly with alkynes in a number of organic solvents examined, and attempts at inducing reaction by chloride removal with $Tl[PF_6]$ led to complicated mixtures of many products. However, we were surprised to discover that *mer*-$(Me_3P)_3Ir(H)(H)(Cl)$ is water-soluble (to the extent of over 4 g in 100 mL, approximately 0.1 M) and is quite reactive in aqueous solution. Thus, reactions between alkynes and *mer*-$(Me_3P)_3Ir(H)(H)(Cl)$ in water lead to the smooth production of *mer*-$(Me_3P)_3Ir(H)(vinyl)(Cl)$ complexes (eq 2).[10]



(2)

We have carried out this reaction with a wide variety of alkynes, both terminal and internal, and the insertions always take place into the Ir–H bond trans to PMe_3. Final confirmation of the structure of the insertion products

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(2) A *partial* listing of some approaches using functionalized phosphines: (a) Bartik, T.; Bartik, B.; Hanson, B. E.; Glass, T. E.; Bebout, W. E. *Inorg. Chem.* **1992**, *31*, 2667. (b) Toth, I.; Hanson, B. E. *J. Mol. Catal.* **1992**, *71*, 365. (c) Renaud, E.; Russell, R. B.; Fortier, S.; Brown, S. J.; Baird, M. C. *J. Organomet. Chem.* **1991**, *419*, 403. (d) Sinou, D.; Safi, M.; Claver, C.; Masdeu, A. *J. Mol. Catal.* **1991**, *68*, L9. (e) Darensbourg, D. J.; Bischoff, C. J.; Reibenspies, J. H. *Inorg. Chem.* **1991**, *30*, 1144. (f) Darensbourg, D. J.; Joo, F.; Kannisto, M.; Katho, A.; Reibenspies, J. H. *Organometallics* **1990**, *11*, 1990. (g) Toth, I.; Hanson, B. E.; Davis, M. E. *Tetrahedron: Asymmetry* **1990**, *1*, 913. (h) Toth, I.; Hanson, B. E.; Davis, M. E. *Catal. Lett.* **1990**, *5*, 183. (i) Benyei, A.; Joo, F. *J. Mol. Catal.* **1990**, *58*, 151. (j) Herrmann, W. A.; Kellnar, J.; Riepl, H. *J. Organomet. Chem.* **1990**, *389*, 103. (k) Herrmann, W. A.; Kulpe, J. A.; Konkol, W.; Bahrmann, H. *J. Organomet. Chem.* **1990**, *389*, 85. (l) Casalnuovo, A. L.; Calabrese, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 4324. (m) Herrmann, W. A.; Kulpe, J. A.; Kellnar, J.; Riepl, H.; Bahrmann, H.; Konkol, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 391. (n) Kuntz, E. G. *CHEMTECH* **1987**, *17*, 570. (o) Larpent, C.; Patin, H. *J. Organomet. Chem.* **1987**, *335*, C13. (p) Sinou, D.; Amrani, Y. *J. Mol. Catal.* **1986**, *36*, 319. (q) Benhamza, R.; Amrani, Y.; Sinou, D. *J. Organomet. Chem.* **1985**, *288*, C37. (r) Amrani, Y.; Sinou, D. *J. Mol. Catal.* **1984**, *24*, 231. (s) Smith, R. T.; Ungar, R. K.; Sanderson, L. J.; Baird, M. C. *Organometallics* **1983**, *2*, 1138.

(3) (a) Hillmyer, M. A.; Lepetit, C.; McGrath, D. V.; Novak, B. M.; Grubbs, R. H. *Macromolecules* **1992**, *25*, 3345. (b) McGrath, D. V.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1991**, *113*, 3611. (c) Novak, B. M.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7542.

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(9) $[Ir(COD)(PMe_3)_3]Cl$ (2.78 g, 4.93 mmol) was heated for 3 h at 100 °C in 20 mL of mesitylene under an atmosphere of dihydrogen. Removal of solvent and washing the crude mixture with pentane yielded 2.13 g (4.65 mmol, 94.3% yield) of *mer*-$(Me_3P)_3Ir(H)(H)(Cl)$. Anal. Calcd (found) for $C_9H_{29}ClP_3Ir$: C, 23.60 (23.38); H, 6.40 (6.12). ^1H NMR (methylene chloride-d_2): δ −24.1 (m, J_{H-P} = 11 Hz, J_{H-H} = 5.6 Hz, 1H), −11.2 (dtd, $J_{H-P_{trans}}$ = 135 Hz, $J_{H-P_{cis}}$ = 22.2 Hz, J_{H-H} = 5.6 Hz, 1H), 1.63 (vt, sep 4.8 Hz, 18H of trans PMe_3), 1.55 (d, J_{H-P} = 11.1 Hz, 9 Hz of cis PMe_3). ^{31}P NMR (methylene chloride-d_2): δ −48.44 (t, J_{P-P} = 54.5 Hz, 1P of cis PMe_3), −42.6 (d, J_{P-P} = 54.5 Hz, 2P of trans PMe_3). ^{13}C NMR (methylene chloride-d_2): δ 22.48 (t, J_{C-P} = 66.3 Hz, 6C of trans PMe_3), 20.09 (d, J_{C-P} = 104.2 Hz, 3C of cis PMe_3).

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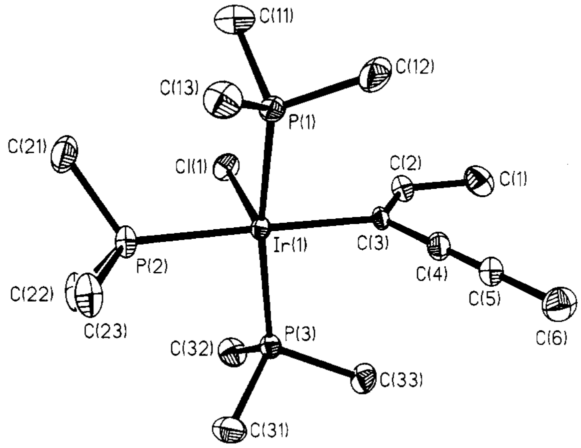

Figure 1. Molecular structure of *mer*-$(Me_3P)_3Ir(H)\{C(H){=}C(H){-}C{\equiv}C{-}Me\}(Cl)$. Important bond lengths (Å): Ir(1)—C(3), 2.146(10); Ir(1)—P(1), 2.314(3); Ir(1)—P(2), 2.328(3); Ir(1)—P(3), 2.319(3); Ir(1)—Cl(1), 2.541(3).

was obtained from a crystal structure determination of one of the complexes derived from the addition of 2,4-hexadiyne (Figure 1).[11]

Having a cis vinyl hydride arrangement on the metal center following alkyne insertion would suggest that *mer*-$(Me_3P)_3Ir(H)(H)(Cl)$ might function as a hydrogenation catalyst. Indeed, this is the case, but it only displays catalytic activity in aqueous solution: there is no activity in organic solvents. *mer*-$(Me_3P)_3Ir(H)(H)(Cl)$ will catalyze the hydrogenation of alkynes to alkanes with alkenes as intermediates and will catalyze the hydrogenation of alkenes to alkanes.[12]

The fact that alkyne insertion into an Ir–H bond of *mer*-$(Me_3P)_3Ir(H)(H)(Cl)$ is only observed in water and that catalytic hydrogenation activity is only observed in water led us to investigate the nature of the water/complex interaction and to discover why *mer*-$(Me_3P)_3Ir(H)(H)(Cl)$ is water-soluble. The ^1H NMR spectrum of *mer*-$(Me_3P)_3Ir(H)(H)(Cl)$ in D_2O shows that there are *two* species in aqueous solution, both displaying similar features: a doublet of triplets in the region around δ-10 ppm and a quartet of doublets in the region of δ-20 ppm.[13] These data show that both compounds have a meridional arrangement of PMe_3 ligands a cis arrangement of the two hydride ligands. This leaves the sixth coordination site as the only point of difference between the two solution species. We speculate that one of the solutions species may be the aquoiridium species $[$*mer*-$(Me_3P)_3Ir(H)(H)(OH_2)]^+$, formed by dissociation of the chloride ligand.[14] The other solution species may be neutral *mer*-$(Me_3P)_3Ir(H)(H)(Cl)$ rendered water-soluble by hydrogen-bonding and dipolar interactions. The enhanced activity in water may result from the ability of water to hydrate and stabilize both the iridium cation and the chloride anion, making chloride dissociation facile. The mismatch between the relatively hard aquo ligand and the relatively soft iridium center allows for the alkyne or alkene to compete effectively with water for that open coordination site. What we do know at this time is that H/D exchange occurs between the hydride ligands of *mer*-$(Me_3P)_3Ir(H)(H)(Cl)$ and D_2O, with the hydride trans to PMe_3 exchanging rapidly (complete within 1 h) and the hydride trans to Cl exchanging more slowly (complete within 24 h). We are continuing to investigate this intriguing system with the goals of elucidating the nature of the species that exist in aqueous solution and determining the full scope of the activity of this complex in water.

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Supplementary Material Available: Listings of NMR data for some *mer*-$(Me_3P)_3Ir(H)(vinyl)(Cl)$ complexes and tables of complete experimental details for the X-ray structural determination, atomic coordinates, bond lengths and angles, anisotropic displacement coefficients, and H-atom coordinates of *mer*-$(Me_3P)_3Ir(H)\{C(H){=}C(H){-}C{\equiv}C{-}Me\}(Cl)$ (6 pages). Ordering information is given on any current masthead page.

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(10) The vinyliridium hydride complexes formed in this study are completely water-soluble if the starting alkyne is water-soluble. If the starting alkyne is not water-soluble, the vinyl products are only partially water-soluble. The synthesis and characterization of the *tert*-butylacetylene addition product is described here as an example. *mer*-$(Me_3P)_3Ir(H)(H)Cl$ (0.400 g, 0.9 mmol) and 244 μL (1.98 mmol) of *tert*-butylacetylene were allowed to react in 14 mL of water. Removal of water under reduced pressure yielded 0.380 g of *mer*-$(Me_3P)_3Ir(H)(CH{=}C(H)(^tBu))$ (0.7 mmol, 78.0% yield). Anal. Calcd (found) for $C_{15}H_{39}P_3ClIr$: C, 33.36 (32.82); H, 7.28 (7.35). ^1H NMR (CD_2Cl_2): δ −23.9 (q, J_{H-P} = 16.9 Hz, 1H), 0.95 (s, 9H, C*Me*$_3$), 1.45 (vt, sep 4.3 Hz, 18H of trans PMe_3), 1.52 (d, J_{H-P} = 7.6 Hz, 9H of cis PMe_3), 6.7 (ddt, J_{H-H} = 17.5 Hz, $J_{H-P_{trans}}$ = 3.5 ppm, $J_{H-P_{cis}}$ = 3.5 Hz, 1H, vinyl IrC*H*), 5.33 (ddt, J_{H-H} = 17.5 Hz, $J_{H-P_{trans}}$ = 7.0 Hz, $J_{H-P_{cis}}$ = 2.7 Hz, 1H, vinyl Me_3CC*H*). ^{31}P NMR (CD_2Cl_2): δ −42.3 (d, J_{P-P} = 65 Hz, 1P of cis PMe_3), −51.4 (t, J_{P-P} = 65 Hz, 2P of trans PMe_3). ^{13}C NMR (CD_2Cl_2): δ 16.6 (t, J_{C-P} = 74.9 Hz, 6C of trans PMe_3), 21.5 (d, J_{C-P} = 108.22 Hz, 3C of cis PMe_3), 29.9 (s, 3C of C*Me*$_3$), 37.3 (s, 1C of *C*Me_3), 128.3 (t, J_{C-P} = 15.0 Hz, 1C of vinyl *C*(H)-CMe_3), 149.0 (s, 1C of vinyl Ir*C*H). Some data for other vinyl complexes can be found in the supplementary material.

(11) The most suitable crystals for X-ray analysis were obtained for the 2,4-hexadiyne adduct: space group $P2_12_12_1$ with a = 11.827(3) Å, b = 12.535(3) Å, c = 14.506(3) Å, V = 2150.6(9) Å^3, and d_{calcd} = 1.655 M g/m^3 for Z = 4. Data refinement was carried out for 1972 observed reflections to convergence with R = 0.0299 and wR = 0.0366. Full details can be found in the supplementary information.

(12) Full details on the hydrogenation chemistry will be provided in a separate paper, but after 24 h at 60 °C and 400 psi H_2, most alkynes studied were completely hydrogenated to the alkane with 5 mol % iridium complex (i.e. 20 turnovers based on alkyne, 40 turnovers based on H_2).

(13) The ^1H NMR spectrum of *mer*-$(Me_3P)_3Ir(H)(H)(Cl)$ in D_2O displays resonances in the hydride region at δ −25.4 (overlapping quartets) and −10.5 ppm (doublet of triplets of doublets) for one of the species and at δ −29.5 (overlapping quartets) and −9.5 ppm (doublet of triplets of doublets) for the other. The ^{31}P NMR spectrum in D_2O displays resonances at δ −48.9 (triplet) and −44.0 ppm (doublet) for the first species and at δ −43.8 (triplet) and −39.4 (doublet) for the second.

(14) A number of aquo/phosphine complexes of iridium have been characterized: (a) Johnson, T. J.; Hauger, B. E.; Lobkovsky, E. B.; Caulton, K. G. *J. Organomet. Chem.* **1992**, *424*, 371–80. (b) Luo, X. L.; Schulte, G. K.; Crabtree, R. H. *Inorg. Chem.* **1990**, *29*, 682. (c) Bauer, H.; Nagel, U.; Beck, W. *J. Organomet. Chem.* **1985**, *290*, 219. (d) Crabtree, R. H.; Lavin, M. *J. Chem. Soc., Chem. Commun.* **1985**, 794.