

Synthesis and Reactions of Hydrido(η^1 -allyl)- and Hydrido(η^3 -allyl)iridium Complexes

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Received February 11, 1985

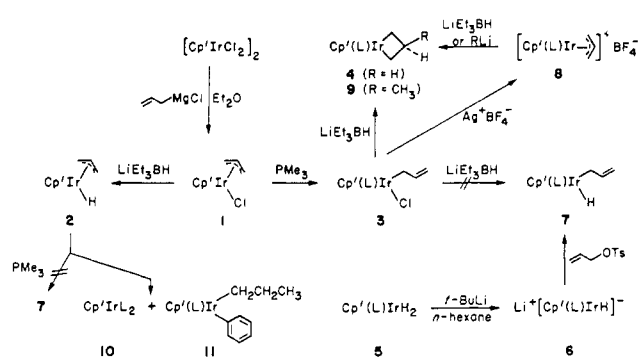
Hydrido(allyl)metal complexes have often been postulated as transient intermediates in organometallic reactions, especially those in which rearrangement of strained rings and alkene isomerization are involved.¹ We wish to report a single system in which isolable hydrido σ - and π -allyl complexes² can be prepared and their interconversions investigated. Several of our results are surprising in themselves, as well as in relation to the types of pathways attributed to closely related intermediates postulated in silica-supported reactions.³

We have successfully prepared the η^1 - and η^3 -allyl complexes 1, 2, 3, and 7 illustrated in the center of Scheme I. Addition of allylmagnesium chloride to an ethereal solution of $[\text{Cp}'\text{IrCl}_2]_2$ ($\text{Cp}' = \eta^5\text{-C}_5\text{Me}_5$)⁴ resulted in the formation of yellow needles of $\text{Cp}'(\eta^3\text{-allyl})\text{chloroiridium}$ (1) in 50–55% yields after crystallization from toluene/hexane.⁵ Our plan was to treat this material with a nucleophilic hydride donor to produce the corresponding η^3 -allyl hydride and with phosphine followed by hydride again to generate the phosphine-substituted η^1 -allyl hydride. As shown in Scheme I, the first step in each of these sequences proceeded as expected: treatment of 1 with lithium triethylborohydride in diethyl ether at room temperature led to $\text{Cp}'(\eta^3\text{-allyl})\text{hydrido-iridium}$ (2) in 30–60% yield. In a similarly straightforward experiment, treatment of 1 with 10–15 equiv of PMe_3 at room temperature in toluene for 15 h led to η^1 -allyl chloride 3 in 60–75% yield.

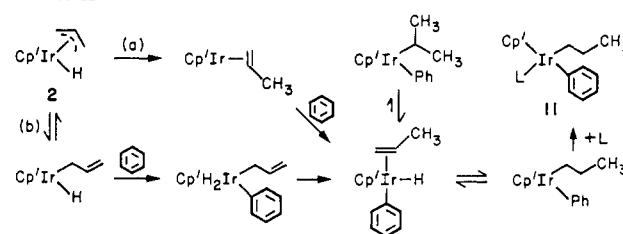
In both cases, further transformations led to unexpected reactions. We discuss first the chemistry of chloro η^1 -allyl complex 3. Treatment of 3 with lithium triethylborohydride gave iridacyclobutane 4 in 50–65% yield after crystallization from *n*-pentane.⁶ None of the η^1 -allyl hydride 7 was detected upon monitoring the reaction by ^1H NMR.

The most likely mechanisms for this transformation are the following: (a) formation of the η^3 -allyl hydride 2, followed by its rapid rearrangement to metallacycle and re-coordination of phosphine; (b) formation of the η^1 -allyl hydride, which rearranges to the metallacycle more rapidly than it is formed; (c) ionization of chloride to give a cationic (η^3 -allyl)iridium intermediate, followed by attack of hydride on the central carbon of the allyl group, as has been observed for cationic molybdenum, tungsten, and (more recently) rhodium complexes.⁶ Possibility (a) is easily ruled out using our independent synthesis of the η^3 -allyl hydride 2; although this material exhibits interesting chemistry on treatment with PMe_3 (see below), under no conditions we have tried is it converted to metallacycle 4. Possibility (b) was tested by working out an alternative synthesis of the η^1 -allyl hydride. This was

Scheme I



Scheme II



accomplished by first deprotonating $\text{Cp}'(\text{L})\text{IrH}_2$ (5, $\text{L} = \text{PMe}_3$) with *tert*-butyllithium in hexane⁷ to give the reactive lithium hydrido-iridate 6. Treatment of 6 with allyl *p*-toluenesulfonate⁸ gave the sensitive hydrido η^1 -allyl complex 7. Purification of this material by chromatography on Al_2O_3 under air-free conditions at -70°C gave 29–33% yields of pure 7 as a light brown oil. Neither heating nor irradiation of 7 gave metallacycle 4.

Having reasonably demonstrated that pathways (a) and (b) were not operating, pathway c was explored. Addition of silver tetrafluoroborate in diethyl ether to chloro η^1 -allyl complex 3 resulted in the immediate formation of silver chloride and a 47% yield of $\text{Cp}'(\text{L})(\eta^3\text{-allyl})\text{iridium tetrafluoroborate}$ (8). Addition of LiEt_3BH to 8 in diethyl ether did give 4 as the exclusive product by ^1H NMR. In addition, use of methylolithium in place of LiEt_3BH resulted in the production of only one of the possible stereoisomers⁹ of the methyliridacyclobutane 9 in 78% yield. This result makes a chloride ionization pathway such as (c) a likely candidate for the formation of the iridacyclobutane 4.

Above it was mentioned that treatment of η^3 -allyl hydride 2 with PMe_3 leads neither to η^1 -allyl complex 7 nor to metallacycle 4. Addition of 4–5 equiv of trimethylphosphine to 2 in benzene at 70°C resulted instead in the formation of two new complexes, separable by chromatography on silica gel. The major component (90%, 65% isolated) was identified as $\text{Cp}'(\text{L})\text{Ir}(\eta^3\text{-Pr})(\text{Ph})$ (11), the product resulting from a combination of benzene C–H activation and propene/M–H insertion. The minor component (10%) was $\text{Cp}'\text{Ir}(\text{PMe}_3)_2$ (10). Despite its similarity to well-known complexes in the cobalt and rhodium series,¹⁰ the latter material has apparently not previously been synthesized. It may be obtained in substantially better yield (90%; 74% after recrystallization) by ultraviolet irradiation of 2 in the presence of 40 equiv of trimethylphosphine in either benzene or hexane. Under these photolytic conditions, no reaction with benzene is observed. Two likely mechanisms for the conversion of 2 to 11 are shown in Scheme II.

In summary, in compound 2 the reactivity of allyl and hydride ligands leads to coordinated propene and provides an open co-

(1) See, for example: (a) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4201. (b) Sherman, E. O.; Olson, M. *J. Organomet. Chem.* **1979**, *172*, C13.

(2) For other studies of allylmetal complexes, see ref 1a,b and: (a) Thorn, D. L. *Organometallics* **1982**, *1*, 879. For a recent report of a bis(η^3 -allyl)-hydridorhenium complex, see: (b) Baudry, D.; Cormier, J. M.; Ephritikhine, M.; Felkin, H. *J. Organomet. Chem.* **1984**, *277*, 99.

(3) (a) Ward, M. D.; Schwartz, J. *J. Mol. Catal.* **1981**, *11*, 397. (b) Kitajima, N.; Schwartz, J. *J. Am. Chem. Soc.* **1984**, *106*, 2220. (c) Ward, M. D.; Schwartz, J. *Organometallics* **1982**, *1*, 1030. (d) Ward, M. D.; Schwartz, J. *J. Am. Chem. Soc.* **1981**, *103*, 5253. (e) Schwartz, J., private communication.

(4) This reaction was modified from that reported in: Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

(5) Rubetzhov, A. Z.; Ivanov, A. S.; Gubin, S. P. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1974**, *23* (11), 2565.

(6) (a) Ephritikhine, M.; Green, M. L. H.; Mackenzie, R. E. *J. Chem. Soc., Chem. Commun.* **1976**, 619. (b) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7272.

(7) Gilbert, T. M.; Bergman, R. G. *J. Am. Chem. Soc.*, in press.

(8) The initial experiments on this reaction were performed by Thomas Gilbert in these laboratories.

(9) We assume the incoming group attacks anti to the C_5Me_5 ring, as observed in the analogous rhodium complex.^{6b}

(10) (a) Klingert, B.; Werner, H. *Chem. Ber.* **1983**, *116*, 1450. (b) Werner, H.; Heiser, B.; Klingert, B.; Dörfel, J. *J. Organomet. Chem.* **1982**, *240*, 179.

ordination site for entry of both stabilizing (e.g., phosphine) and reactive (e.g., benzene) ligands into the coordination sphere of the metal. In the intermediate formed immediately after the oxidative addition of benzene, the propene ligand serves as a "trap" for the metal-bound hydrogen, thus preventing reextrusion of benzene. Our results provide direct support for many alkene activation and isomerization mechanisms that have been postulated in the past.¹ However, these observations contrast strongly with mechanisms proposed for hydrido(allyl)metal complexes bound to silica.³ Attached to the support, hydrido(allyl) complexes are suggested to coordinate 2 mol of phosphine without either η^3 - η^1 isomerization or reductive elimination of propene. Perhaps most strikingly, exposure of the silica-supported hydrido(allyl) complexes to arenes produces catalytic arene hydrogenation—i.e., a reaction which leaves the hydrido(allyl) functionality intact—rather than decoordination, arene C–H activation, and alkene insertion, as we observe in our homogeneous system. We hope an understanding of the physical causes of these profound differences in reactivity will be achieved by continuing the direct study of the supported materials and pursuing the study of homogeneous models for such systems.

Acknowledgment. We are grateful to Prof. Jeffrey Schwartz for helpful discussions and disclosure of results prior to publication. This work was supported by the Director, Office of Basic Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

Supplementary Material Available: Spectral and analytical data for the compounds 1–4 and 7–11 (3 pages). Ordering information is given on any current masthead page.

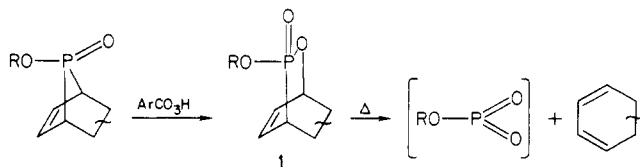
Metaphosphate and Metaphosphonic Anhydride Formation by Thermolysis of 5,6-Oxaphosphabicyclo[2.2.2]octenes: Electrophilic α -Substitution on a Pyrrole

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Received February 11, 1985

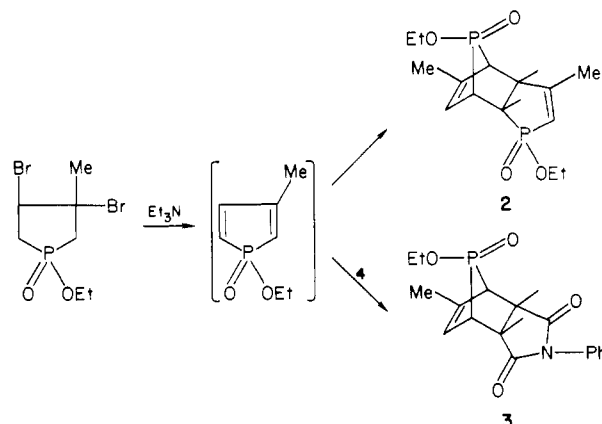
We showed in earlier work¹ that a variety of cyclic phosphine oxides with highly contracted C–P–C angles readily undergo O-insertion into a C–P bond with peroxy acids. We have now found that strained cyclic phosphinates can undergo the same reaction and are converted to cyclic phosphonates. Of special interest are the phosphonates 1 arising from O-insertion into the 7-phosphanorbornene (7-PNB) framework, for these structures can in principle undergo fragmentation by retro-[4 + 2] cycloaddition to form the metaphosphate species ROPO_2 . Meta-



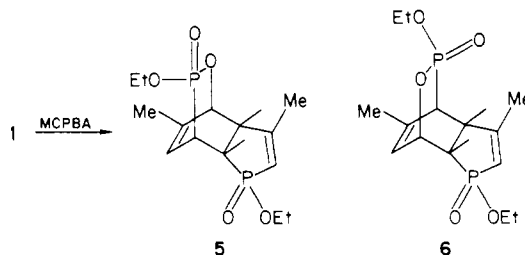
phosphates (and other low-coordination phosphorus species²) are of great current interest; the recently reviewed³ pioneering work of F. H. Westheimer and associates has demonstrated that this highly reactive, polymerizable species has a momentary existence as a monomer and can be trapped with suitable reagents. We indeed have found that the thermolysis of the 5,6-oxaphosphabicyclo[2.2.2]octene system 1 opens a new and useful route to

metaphosphates. The temperature for generating this species is relatively low (100–110 °C), suggesting that practical applications may be derived from the high reactivity of the metaphosphates. In exploring this possibility, we have encountered a valuable property of metaphosphates that was suggested by their known⁴ ability to perform electrophilic substitution on aniline derivatives: N-substituted pyrroles are highly effective trapping agents for metaphosphates and are phosphorylated specifically at the α -position.

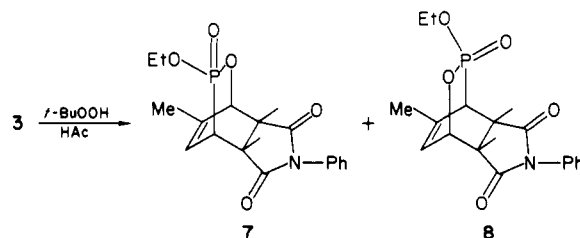
We have employed the 7-PNB phosphinates 2 and 3 in this



work. The former results from dimerization⁵ of 1-ethoxy-3-methylphosphole oxide on formation, while 3 (mp 219–220 °C; δ ³¹P NMR (CDCl_3) +80.1) is formed when the phosphole is generated in the presence of N-phenylmaleimide (4). Phosphinate 2 reacted completely in 18 h with *m*-chloroperbenzoic acid (MCPBA) at 25 °C, providing only one of the two possible O-insertion products 5 and 6. The correct structure was easily



assigned from its ³¹P NMR spectrum (phosphonate δ +27.2, phosphine oxide δ +67.2), which had signal splitting (63.5 Hz) clearly derived from the three-bond ³¹P–³¹P connection of 5. A purification procedure consisting of complexation of the benzoic acid with solid KF, chromatography on Florosil, and recrystallization from benzene–cyclohexane provided analytically pure⁶ 5; attempts to remove the benzoic acid with various bases were less effective.¹ Phosphinate 3 gave a nearly 1:1 mixture of O-insertion products 7 and 8 (δ ³¹P +25.6, +25.7, unassigned) with



(4) Clapp, C. H.; Westheimer, F. H. *J. Am. Chem. Soc.* **1974**, *96*, 6710. Clapp, C. H.; Satterthwait, A.; Westheimer, F. H. *J. Am. Chem. Soc.* **1975**, *97*, 6873.

(5) Usher, D. A.; Westheimer, F. H. *J. Am. Chem. Soc.* **1964**, *86*, 4732.

(6) The ¹³C NMR spectra supported the structure, especially by showing direct attachment of O to bridgehead C (δ 79.3, ²J_{POC} = 7.5, J_{PCC} = 3.0 Hz). Anal. Calcd for C₁₄H₂₂O₅P: C, 50.61; H, 6.67; P, 18.61. Found: C, 50.45; H, 6.75; P, 18.41.

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(2) Regitz, M.; Maas, G. *Top. Curr. Chem.* **1981**, *97*, 71.

(3) Westheimer, F. H. *Chem. Rev.* **1981**, *81*, 313.