Articles

Divergent Isomerization Behavior and Rhodium(I) Coordination Chemistry of Indenyl Ligands Bearing either One or Two Pnictogen Donor Fragments

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1-(Diphenylphosphino)-2-(dimethylamino)indene (**2c**) has been prepared in 61% yield and upon exposure to Al_2O_3 is mostly isomerized to 3-(diphenylphosphino)-2-(dimethylamino)-indene (**2d**) (**2c**:**2d** ≈ 1:3); similarly, 1-(diisopropylphosphino)-2-(dimethylamino)indene (**2a**) is only partially converted to the corresponding C3 isomer (**2b**) upon treatment with Al_2O_3 (**2a**:**2b** ≈ 3:1). In contrast, 1-(diisopropylphosphino)indene (**6a**) has been prepared in 92% yield and is easily converted to 3-(diisopropylphosphino)indene (**6b**) on passing over Al_2O_3; 0.5 equiv of $[(\eta^4\text{-COD})RhCl]_2$ and **6b** combine to give $[(\kappa^1\text{-}P\text{-}\mathbf{6b})(\eta^4\text{-COD})RhCl]$ (**7**) in 79% yield. Treatment of either 2-(dimethylamino)indene (**1**) or **6b** with a stoichiometric amount of *n*-BuLi, followed by the addition of 0.5 equiv of $[(\eta^4\text{-COD})RhCl]_2$, produces the ($\eta^5$-indenyl)-rhodium(I) complexes **8** (53% yield) and **9** (88% yield), respectively, in which the pnictogen donor is apparently not coordinated to the rhodium center. When 2.5 equiv of *n*-BuLi is combined with **6b** and subsequently treated with 0.5 equiv of $[(\eta^4\text{-COD})RhCl]_2$, **9** is also produced, along with a small amount of the unusual Rh_2Li_2 species **10**. The crystallographically determined structures of **2d**, **3**·C_6H_6, **7**, and **10**·C_7H_8 are reported.

Introduction

Transition-metal complexes supported by π-coordinated η^5-indenyl ligands have a longstanding history in the field of organometallic chemistry and continue to figure importantly in current research.[1] In particular, main-group-functionalized indenyl ligands have attracted considerable attention,[2] since they have been shown to impart interesting reactivity properties to both early- and late-transition-metal fragments.[3] Recently we reported the synthesis of the P,N-functionalized indene **2a** and demonstrated that this versatile ligand system can be used in the preparation of neutral (**3**), cationic (**4**), and zwitterionic (**5**) Rh(I) complexes (Scheme 1); compounds **4** and **5** have been shown to catalyze the dehydrogenative coupling of triethylsilane and styrene.[4] During the course of this study we observed that (a) the clean conversion of **3** into **4** is accompanied by a structural rearrangement of the indene ligand in which the formerly allylic (C1) ^{i}Pr$_2$P substituent is placed at the vinylic (C3) position and (b) in stark contrast to the numerous (η^4-COD)Rh(η^5-indenyl) (COD = 1,5-cyclooctadiene) complexes,[5] the $[(\eta^4\text{-COD})Rh]^+$ fragment in **5** selectively binds in a κ^2-P,N fashion to the periphery of the carbanion generated upon deprotonation of **2a**, rather than coordinating in the usual η^5 manner to the face of the carbocyclic framework. In light of these observations, we became interested in preparing directly the ligand **2b** (i.e. the C3 isomer of **2a**) and in gaining a better understanding of the factors that favor the unusual κ^2 bonding arrangement found in **5**. Herein we

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(1) (a) Calhorda, M. J.; Veiros, L. F. *Coord. Chem. Rev.* **1999**, *185*−*186*, 37. (b) Lobanova, I. A.; Zdanovich, V. I. *Russ. Chem. Rev. (Engl. Transl.)* **1988**, *57*, 967.

(2) Stradiotto, M.; McGlinchey, M. J. *Coord. Chem. Rev.* **2001**, *219*−*221*, 311.

(3) For some recent examples, see: (a) Xie, Z. *Acc. Chem. Res.* **2003**, *36*, 1. (b) Fan, W.; Waymouth, R. M. *Macromolecules* **2003**, *36*, 3010. (c) Lee, M. H.; Han, Y.; Kim, D.; Hwang, J.-W.; Do, Y. *Organometallics* **2003**, *22*, 2790. (d) Kamigaito, M.; Watanabe, Y.; Ando, T.; Sawamoto, M. *J. Am. Chem. Soc.* **2002**, *124*, 9994. (e) Greidanus, G.; McDonald, R.; Stryker, J. M. *Organometallics* **2001**, *20*, 2492.

(4) Stradiotto, M.; Cipot, J.; McDonald, R. *J. Am. Chem. Soc.* **2003**, *125*, 5618.

(5) For some recently reported Rh(η^5-indenyl) complexes, see: (a) Santi, S.; Ceccon, A.; Carli, F.; Crociani, L.; Bisello, A.; Tiso, M.; Venzo, A. *Organometallics* **2002**, *21*, 2679. (b) Santi, S.; Ceccon, A.; Crociani, L.; Gambaro, A.; Ganis, P.; Tiso, M.; Venzo, A.; Bacchi, A. *Organometallics* **2002**, *21*, 565. (c) Schumann, H.; Stenzel, O.; Dechert, S.; Girgsdies, F.; Blum, J.; Gelman, D.; Halterman, R. L. *Eur. J. Inorg. Chem.* **2002**, 211. (d) Rupert, K. C.; Liu, C. C.; Nguyen, T. T.; Whitener, M. A.; Sowa, J. R., Jr. *Organometallics* **2002**, *21*, 144. (e) Westcott, S. A.; Kakkar, A. K.; Taylor, N. J.; Roe, D. C.; Marder, T. B. *Can. J. Chem.* **1999**, *77*, 205.

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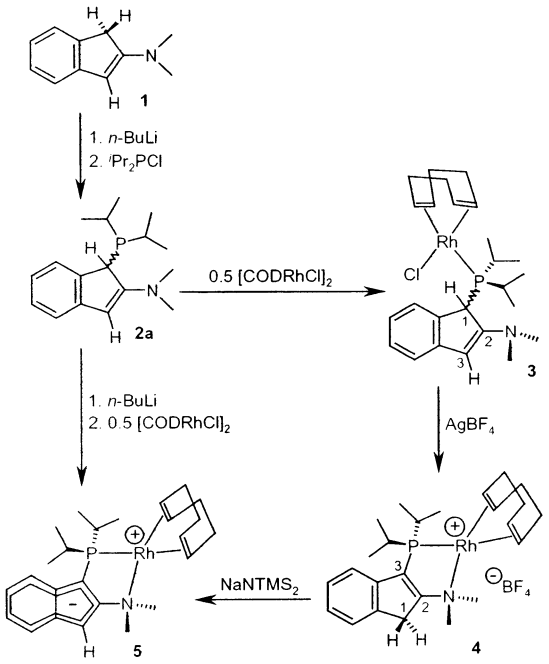
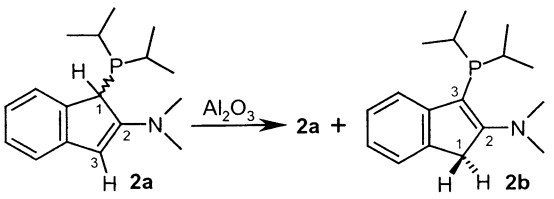
Scheme 1. Synthesis of the P,N-Substituted Indene Ligand 2a and Related Rh(I) Derivatives, Including the Zwitterionic Complex 5



report on our pursuit of these targets, including the crystallographic identification of a new "non-η^5" structural motif for rhodium−indenide complexes.

Results and Discussion

The conversion of **2a** into **2b** (eq 1) was attempted using the method of Anderson and co-workers,[6] who reported that while the isomerization of 1-(diphenylphosphino)indene into 3-(diphenylphosphino)indene occurs slowly on standing in solution, this transformation proceeds rapidly and quantitatively upon exposure to alumina.[7] After stirring a C_6D_6 solution of pure **2a** over alumina for several hours, ^{31}P NMR signals attributable to **2a** (19.6 ppm) and what we presume to be the vinylic isomer (vide infra) **2b** (−2.9 ppm) were observed. Although this transformation appeared to proceed without the formation of byproducts, complete conversion could not be achieved; even after several days the ratio of **2a** to **2b** was found only to be ∼3:1. Efforts to promote this isomerization process by heating a toluene solution of **2a** at 80 °C were also unsuccessful, generating a mixture of **2a**, **2b**, and other phosphorus-containing products.



(1)

Anderson and co-workers also observed that the C1 to C3 isomerization of (diphenylphosphino)indene occurs when the phosphorus center is coordinated to platinum.[6]

(6) Fallis, K. A.; Anderson, G. K.; Rath, N. P. *Organometallics* **1992**, *11*, 885.

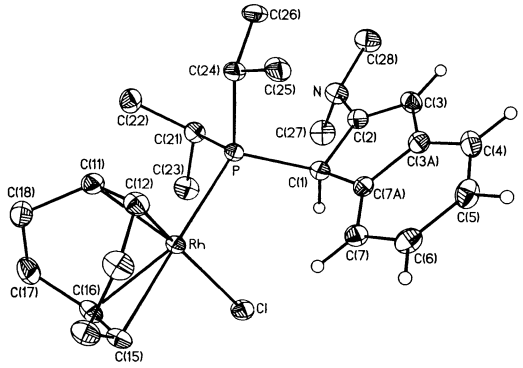


Figure 1. Crystallographically determined structure of **3**·C_6H_6, shown with 40% displacement ellipsoids. Selected hydrogen atoms and the benzene solvate have been omitted for clarity. Selected interatomic distances (Å): Rh−Cl, 2.3774(5); Rh−P, 2.3427(5); Rh−C11, 2.137(2); Rh−C12, 2.115(2); Rh−C15, 2.232(2); Rh−C16, 2.190(2); P−C1, 1.882(2); N−C2, 1.390(3); C1−C2, 1.530(3); C2−C3, 1.351(3). Selected interatomic angles (deg): C2−N−C27, 118.0(2); C2−N−C28, 116.2(2); C27−N−C28, 112.3(2).

The ligand **2a** does not undergo such a structural rearrangement upon coordination to rhodium,[4] as confirmed by the crystallographically determined structure of [(κ^1-*P*,N-**2a**)(η^4-COD)RhCl]·C_6H_6 (**3**·C_6H_6; Figure 1).[8] Selected data for all of the crystallographically characterized compounds reported herein are collected in Table 1. The rhodium center in **3**·C_6H_6 possesses a square-planar geometry commonly observed for Rh(I) (d^8) complexes; as expected, the metrical parameters indicate that the alkene donor (C11, C12) trans to chloride binds more tightly to the metal center than the corresponding alkene (C15, C16) trans to phosphine. Attempts to promote the C1 to C3 isomerization of the indenyl fragment in **3**, either by stirring over alumina or by heating, resulted in decomposition.

In an effort to determine the possible role of the isopropyl substituents on phosphorus in blocking the isomerization of **2a** to **2b**, the related 1-diphenylphosphino-substituted aminoindene **2c** was prepared and its isomerization behavior examined (Scheme 2). Similar to what was observed for **2a**, a C_6D_6 solution of pure **2c** was transformed into a mixture of **2c** and **2d** (∼1:3) after exposure to alumina for several hours. Also similar to the **2a**/**2b** system, attempts to drive this rearrangement process by heating a **2c**/**2d** mixture at 80 °C in toluene were unsuccessful, leading to the formation of numerous phosphorus-containing products.

Although we were unable to efficiently separate **2c** from **2d**, the predominant formation of the latter species in the aforementioned isomerization experiment allowed for ^1H and ^{31}P NMR resonances attributable to **2d** to be assigned. Moreover, in one instance we were able to crystallize minute quantities of **2d** that proved to be suitable for single-crystal X-ray diffraction analysis. The crystallographically determined structure of **2d** is presented in Figure 2 and by analogy provides indirect evidence for **2b**. The overall geometric features in **2d** are comparable to those of 3-(diphenylphosphino)in-

(7) Stradiotto, M.; Kozak, C.; McGlinchey, M. J. *J. Organomet. Chem.* **1998**, *564*, 101.

(8) Although not isomorphous, the molecular geometry and metrical parameters of **3** found in **3**·C_6H_6 are quite similar to those found in **3**·CH_2Cl_2.[4]

Table 1. Crystal Data for 2d, 3·C_6H_6, 7, and 10·C_7H_8

	2d	**3**·C_6H_6	**7**	**10**·C_7H_8
empirical formula	$C_{23}H_{22}NP$	$C_{31}H_{44}ClNPRh$	$C_{23}H_{33}ClPRh$	$C_{53}H_{70}Li_2P_2Rh_2$
formula wt	343.39	600.00	478.82	988.73
cryst dimens	0.34 × 0.14 × 0.08	0.31 × 0.30 × 0.16	0.39 × 0.24 × 0.09	0.34 × 0.22 × 0.20
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$I2/a$
a (Å)	12.518 (1)	14.765 (1)	7.7514 (5)	18.857 (1)
b (Å)	8.2259 (8)	7.9199 (6)	10.6743 (7)	17.4958 (9)
c (Å)	18.445 (2)	25.158 (2)	14.4876 (9)	14.0506 (7)
α (deg)	90	90	75.040 (1)	90
β (deg)	102.876 (2)	105.251 (1)	75.390 (1)	97.527 (1)
γ (deg)	90	90	70.382 (1)	90
V (Å^3)	1851.5 (3)	2838.2 (4)	1072.7 (1)	4595.7 (4)
Z	4	4	2	4
ρ_{calcd} (g cm^{-3})	1.232	1.404	1.482	1.429
μ (mm^{-1})	0.153	0.773	1.000	0.823
2θ limit (deg)	52.82	52.78	52.76	52.74
index ranges	$-15 \le h \le 14$	$-17 \le h \le 18$	$-9 \le h \le 9$	$-22 \le h \le 23$
	$-10 \le k \le 9$	$-9 \le k \le 9$	$-13 \le k \le 13$	$-21 \le k \le 21$
	$-22 \le l \le 22$	$-31 \le l \le 29$	$-18 \le l \le 18$	$-17 \le l \le 11$
total no. of data collected	9517	16 608	6585	11 299
no. of indep rflns	3792	5786	4334	4681
R_{int}	0.0475	0.0232	0.0175	0.0230
abs cor	empirical (SADABS)	empirical (SADABS)	face indexed	empirical (SADABS)
range of transmissn	0.9879−0.9498	0.8864−0.6100	0.9154−0.6964	0.8527−0.7672
no. of data/restraints/params	3792/0/228	5786/0/316	4334/0/235	4681/0/269
R1 ($F_o^2 \ge 2\sigma(F_o^2)$)	0.0491	0.0259	0.0254	0.0320
wR_2 ($F_o^2 \ge -3\sigma(F_o^2)$)	0.1260	0.0690	0.0658	0.0885
goodness of fit	1.016	1.031	1.046	1.050

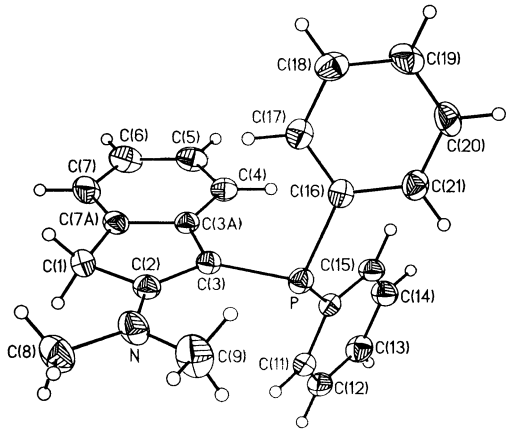
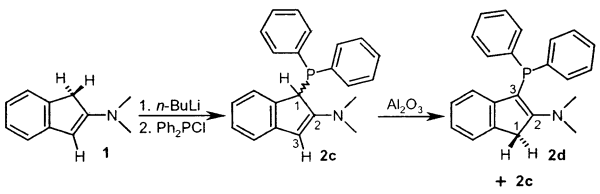


Figure 2. Crystallographically determined structure of **2d**, shown with 40% displacement ellipsoids. Selected interatomic distances (Å): P−C3, 1.807(2); N−C2, 1.352(3); C1−C2, 1.518(3); C2−C3, 1.380(3). Selected interatomic and torsion angles (deg): C2−N−C8, 121.6(2); C2−N−C9, 122.8(2); C8−N−C9, 115.5(2); C1−C2−N−C8, 5.2(3); C3−C2−N−C9, −0.1(4).

Scheme 2. Synthesis and Attempted Isomerization of Compounds 2c and 2d



dene.[6] In addition, the coplanarity of the non-hydrogen atoms (excluding the phenyl substituents on phosphorus)[9] and the short N−C2 distance (1.352(3) Å) indicate that the lone pair of electrons on nitrogen in **2d** is in conjugation with the indene π-system. This bonding scenario provides a possible rationale as to why the isomerization of **2a**/**2b** or **2c**/**2d** over alumina is sluggish, whereas the transformation of 1-(diphenylphosphino)indene[6] or 1-(diisopropylphosphino)indene (**6a**, vide infra) into the corresponding C3 isomer is rapid. In consideration of steric factors alone, it may be that the large R_2P fragment is best accommodated at the allylic (C1) position in either **2a** or **2c**, when the dimethylamino group adopts a coplanar geometry with the indene ring. Furthermore, conjugation of the lone pair on nitrogen should greatly increase the electron density of the indene ring in either **2a** or **2c** and, in doing so, should reduce the acidity of the benzylic hydrogen atom at the C1 position.[10] Since the C1 to C3 isomerization of phosphinoindenes over alumina can be viewed as a deprotonation/reprotonation sequence,[6,7] the increased pK_a of the benzylic proton on going from 1-(diphenylphosphino)indene to either **2a** or **2c** should be manifested in an increased barrier to isomerization. This phenomenon may also have relevance to the rapid C1 to C3 isomerization of the coordinated indene ligand on going from **3** to **4** (Scheme 1). As in **2d**, the short N−C2 distance in **3**·C_6H_6 (1.390(3) Å) suggests that the lone pair of electrons on the uncoordinated dimethylamino group is conjugated with the indene ring, possibly inhibiting the C1 to C3 rearrangement of the bound ligand (**2a**) in **3**.[11] Coordination of the nitrogen donor to rhodium following abstraction of the chloride ligand in **3** would disrupt this conjugation, enabling the isomerization of **2a** to **2b** to proceed within the metal

(9) The mean deviation from the plane defined by C1, C2, C3, C3a, C4, C5, C6, C7, C7a, C8, C9, N, and P in **2d** is less than 0.05 Å. Within error, the sum of the angles around N in **2d** is 360°.

(10) Whereas the pK_a value of the benzylic protons on indene itself is 20.1, the incorporation of a 2-(cyclo-C_4H_8N) substituent causes the pK_a of the benzylic protons to rise to 24.5; see: Bordwell, F. G.; Satish, A. V. *J. Am. Chem. Soc.* **1992**, *114*, 10173.

(11) By comparison, the N−C2 and Rh−P distances in **4** are 1.459(6) and 2.305(1) Å, respectively: Cipot, J.; Abeysekera, D.; Ferguson, M. J.; McDonald, R.; Stradiotto, M. Unpublished results.

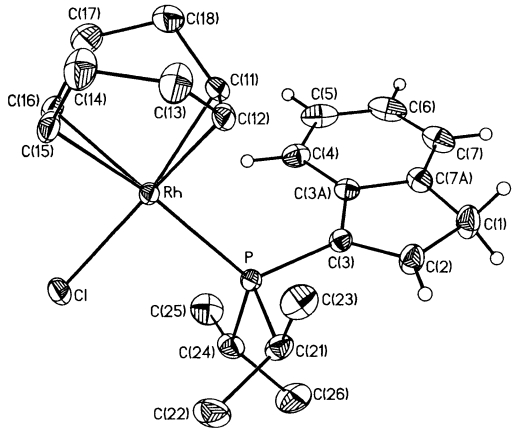
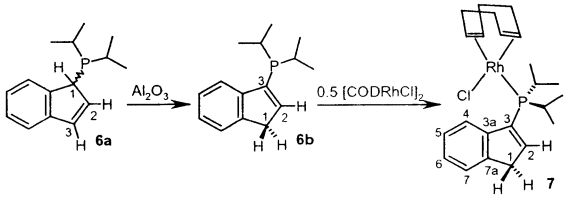


Figure 3. Crystallographically determined structure of **7**, shown with 40% displacement ellipsoids. Selected hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å): Rh−Cl, 2.3589(6); Rh−P, 2.3366(5); Rh−C11, 2.136(2); Rh−C12, 2.124(2); Rh−C15, 2.211(2); Rh−C16, 2.199(2); P−C3, 1.821(2); C1−C2, 1.500(3); C2−C3, 1.344(3).

Scheme 3. Isomerization of 6a to 6b, Followed by Complexation with Rhodium, Producing 7



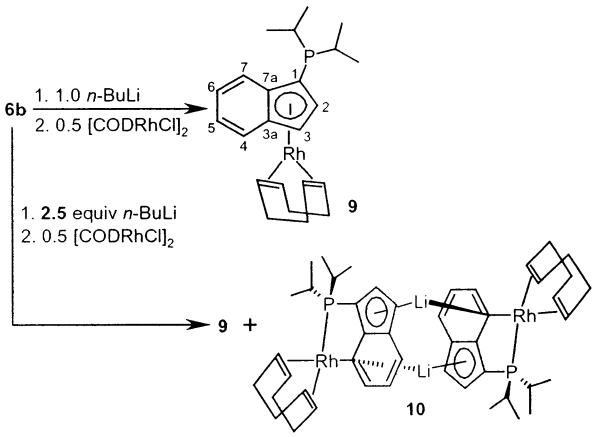
coordination sphere and leading to the exclusive formation of $[(\kappa^2\text{-}P,N\text{-}\mathbf{2b})(\eta^4\text{-COD})\text{Rh}]^+\text{BF}_4^-$ (**4**).[12]

In keeping with the aforementioned arguments, substitution of the 2-dimethylamino fragment in **2a** for a hydrogen atom facilitates the C1 to C3 isomerization process. 1-(Diisopropylphosphino)indene (**6a**) was prepared in 92% yield and in turn was cleanly converted to 3-(diisopropylphosphino)indene (**6b**) upon exposure to alumina (Scheme 3). Treatment of **6b** with 0.5 equiv of $[(\eta^4\text{-COD})\text{RhCl}]_2$ generated the expected coordination complex $[(\kappa^1\text{-}P\text{-}\mathbf{6b})(\eta^4\text{-COD})\text{RhCl}]$ (**7**) in 79% yield. The crystallographically determined structure of **7** is presented in Figure 3 and confirms the presence of the coordinated ligand **6b**. From the perspective of the rhodium coordination sphere, the structural attributes of **7** mirror those of $\mathbf{3}\cdot C_6H_6$ and therefore do not warrant further discussion.

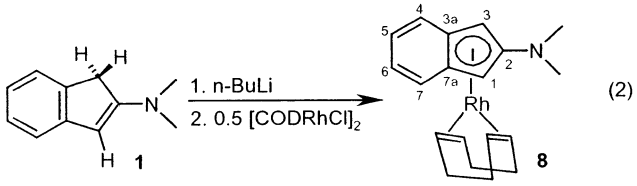
In addition to examining the isomerization behavior of **2a** and related derivatives, studies were conducted in an effort to identify the substitution pattern needed in order to promote the peripheral (rather than facial) binding of indenide ligands to rhodium(I) fragments, as occurs in the unprecedented $[\kappa^2\text{-}P,N]$Rh(I) zwitterion **5** (Scheme 1).[4] Our initial approach was to examine the impact of systematically removing either the diisopropylphosphino or dimethylamino substituents from the precursor, **2a**. Lithiation of **1** followed by treatment with

(12) The related isomerization of phospholes to phospholenes within the coordination sphere of Pd(II) has recently been reported: Leca, F.; Sauthier, M.; le Guennic, B.; Lescop, C.; Toupet, L.; Halet, J.-F.; Réau, R. *Chem. Commun.* **2003**, 1774.

Scheme 4. Generation of the Mononuclear η^5 Complex 9 and the Rh_2Li_2 Species 10



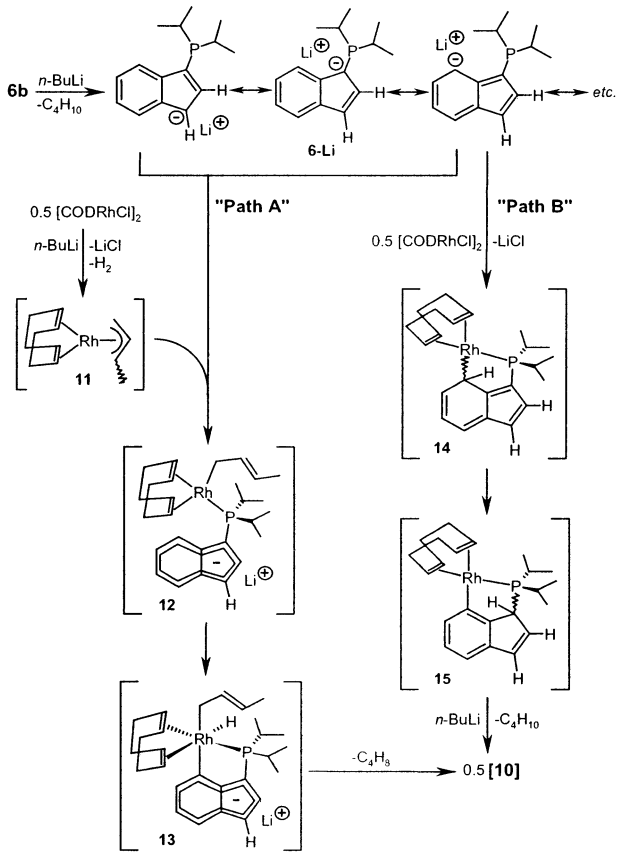
0.5 equiv of $[(\eta^4\text{-COD})\text{RhCl}]_2$ produced the anticipated η^5-indenyl complex, **8**, in 53% yield (eq 2). Similarly,



treatment of **6b** with 1 equiv of *n*-BuLi proceeded cleanly in diethyl ether; in situ monitoring of the reaction (^{31}P NMR) confirmed the consumption of **6b**, accompanied by the appearance of one new phosphorus-containing product (**6-Li**) at −8.9 ppm. Addition of 0.5 equiv of $[(\eta^4\text{-COD})\text{RhCl}]_2$ to the reaction mixture produced the η^5 species **9** as the only phosphorus-containing product ($\delta(^{31}\text{P})$ −11.9), which in turn was isolated in 88% yield (Scheme 4). The lack of rhodium coupling to phosphorus is in keeping with the structural formulation proposed for **9**. These preliminary experiments confirm that the ability of the adjacent phosphorus and nitrogen donors to chelate the Rh(I) center in **5** is critical in order to circumvent η^5 coordination.

In the pursuit of **9**, a reaction was inadvertently carried out in which **6b** was initially treated with excess (2.5 equiv) rather than a stoichiometric quantity of *n*-BuLi. Despite the excess base employed, the clean formation of **6-Li** was noted (^{31}P NMR) and subsequently $[(\eta^4\text{-COD})\text{RhCl}]_2$ (0.5 equiv) was added to the reaction mixture. After approximately 2 h, the consumption of **6-Li** along with the formation of **9** as the major product was observed (^{31}P NMR); the mixture was then filtered and set to crystallize at −30 °C. Although no crystalline material was obtained from this reaction mixture initially, storage for an extended period of time at reduced temperatures ultimately produced a few X-ray-quality crystals. Surprisingly, single-crystal X-ray diffraction analysis revealed that this material was not the anticipated η^5-indenyl complex **9** but rather the unusual dimeric Rh_2Li_2 species **10** (Scheme 4). Reexamination of the resulting supernatant solution by using ^{31}P NMR techniques revealed the previously observed singlet at −11.9 ppm attributable to **9**, along with a number of other rhodium-coupled signals between 49

Scheme 5. Two Possible Mechanistic Routes to 10



and 75 ppm. Efforts to isolate more of **10** from this reaction mixture were in vain. Moreover, all attempts to rationally prepare **10**, either by using the synthetic methodology presented above or via the addition of 1.0 equiv of **6-Li** to a preformed mixture of 0.5 equiv of $[(\eta^4\text{-COD})\text{RhCl}]_2$ and 1.0 equiv of *n*-BuLi (see Scheme 5, path A) were unsuccessful, and so we are presently unable to provide any spectroscopic characterization data for this highly unusual rhodium−indenide complex.

The structure of **10**·C_7H_8 is presented in Figure 4 and is comprised of a dimeric pair of rhodium-substituted lithium indenide fragments that are related by a crystallographically imposed center of inversion. Each of the $[(\eta^4\text{-COD})\text{Rh}]$ fragments in **10** is coordinated both to a pendant phosphine donor and to the C7 position within a single indenide ring. In turn, the lithium atoms serve to bridge the halves of **10**, bonding to the C_5 unit of one indenide fragment and to the C7 carbon of the adjacent indenide unit. The Rh−P distance in **10** (2.3536(6) Å) is comparable to those found in the related phosphinoindene complexes **3**, **4**, and **7**.[4,11] In contrast, the P−C1 bond in **10** (1.765(3) Å) is contracted significantly relative to the related distances in **3**, **4**, and **7**[4,11] and is best compared to the $P-C_{\text{indenide}}$ bond in the zwitterionic complex **5** (1.758(2) Å).[4]

In an attempt to rationalize the formation of **10**, we tentatively propose two simplified mechanistic pathways (**A** and **B**), which are outlined in Scheme 5; other equally viable routes to **10** could also be envisioned. One of the proposed mechanistic pathways (**A**) begins with the reaction of $[(\eta^4\text{-COD})\text{RhCl}]_2$ with the excess *n*-BuLi remaining after the formation of **6-Li**, presumably

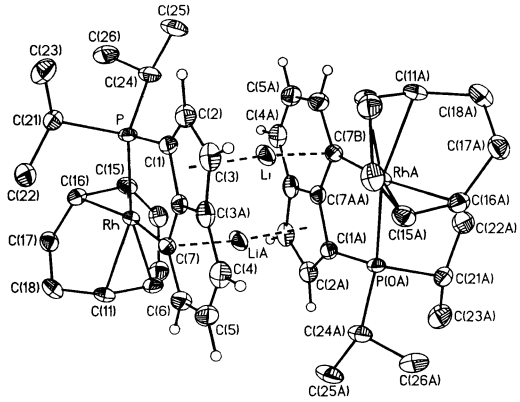


Figure 4. Crystallographically determined structure of **10**·C_7H_8, shown with 40% displacement ellipsoids. Selected hydrogen atoms and the toluene solvate have been omitted for clarity. Selected interatomic distances (Å): Rh−P, 2.3536(6); Rh−C7, 2.093(3); Rh−C11, 2.161(3); Rh−C12, 2.198(3); Rh−C15, 2.198(3); Rh−C16, 2.233(3); P−C1, 1.765(3); Li−C1, 2.264(5); Li−C2, 2.257(5); Li−C3, 2.267(5); Li−C3a, 2.306(5); Li−C7a, 2.293(5); Li−C7B*, 2.193(5); C1−C2, 1.422(4); C2−C3, 1.388(4); C3−C3a, 1.420(4); C3a−C4, 1.420(4); C4−C5, 1.364(5); C5−C6, 1.414(4); C6−C7, 1.400(4); C7−C7a, 1.424(4); C7a−C1, 1.428(4) (*C7B is the position related to C7 via the crystallographic inversion center).

leading to $(\eta^4\text{-COD})\text{Rh}(n\text{-Bu})$ upon loss of LiCl; a sequence of β-hydride elimination, C−H oxidative addition, and H_2 reductive elimination steps could then produce **11**.[13] Coordination of rhodium to the phosphine unit of **6-Li**, as in **12**, followed by insertion into the C7−H bond would generate the Rh(III) intermediate **13**. Reductive elimination of 2-butene, followed by dimerization, then generates **10**. An alternative mechanistic pathway (**B**) has $[(\eta^4\text{-COD})\text{RhCl}]_2$ reacting directly with **6-Li** at the C7 position, producing **14**. Subsequent rearrangement to **15** reestablishes the aromaticity of the C_6 ring, and reaction with the excess *n*-BuLi present, followed by dimerization, produces **10**.

Conclusions

From the experimental data presented in this report, it is evident that the isomerization behavior of indenes bearing only *one* group 15 donor can differ significantly from indenes containing *two adjacent* group 15 substituents; whereas 1-(diisopropylphosphino)indene is easily transformed into 3-(diisopropylphosphino)indene, the introduction of a 2-dimethylamino substituent greatly inhibits this rearrangement process. The synthetic work reported herein also demonstrates that while a lithiated indene bearing adjacent diisopropylphosphino and dimethylamino substituents has been shown to form an unusual zwitterionic κ^2-*P*,*N*-indenide complex of rhodium(I),[4] removal of either of these group 15 fragments results in the formation of the corresponding pnictogen-substituted $(\eta^5$-indenyl)rhodium(I) species, in which the pendant group 15 donor is apparently not involved in bonding to rhodium. With this key design feature in mind, we are currently examining a series of bidentate ligand precursors structurally related to **2a** that incor-

(13) The formation of **11** has been reported: (a) Fryzuk, M. D. *Inorg. Chem.* **1982**, *21*, 2134. (b) Stuehler, H. O.; Mueller, J. *Chem. Ber.* **1979**, *122*, 1359.

porate a diversity of p-block donors. Reports pertaining to the use of these in the preparation of neutral, cationic, and zwitterionic transition-metal complexes are forthcoming.

Experimental Section

General Considerations. All manipulations were conducted in the absence of oxygen and water under an atmosphere of dinitrogen, either by using standard Schlenk methods or within an Innovative Technologies glovebox apparatus,[14] utilizing glassware that was oven-dried (130 °C) and evacuated while hot prior to use. Celite (Aldrich) was oven dried (130 °C) for 5 days and then evacuated for 24 h prior to use. Diethyl ether, pentane, and toluene were dried and deoxygenated by refluxing for a minimum of 24 h under a flow of dinitrogen, in the presence of sodium wire. Benzophenone was added to the solvent/drying agent mixture in order to provide visual confirmation (i.e. the observed persistence of the benzophenone ketyl) that an appropriate level of purification had been achieved. The solvents used within the glovebox were stored over activated 3 Å molecular sieves. C_6D_6 (Aldrich) was degassed by using three repeated freeze−pump−thaw cycles and then dried over 3 Å molecular sieves for 24 h prior to use. $CDCl_3$ (Aldrich) was degassed by using three repeated freeze−pump−thaw cycles, dried over CaH_2 for 7 days, and distilled in vacuo. $^{i}Pr_2PCl$, Ph_2PCl, and *n*-BuLi (1.6 M in hexanes) were obtained from Aldrich and were used as received, while $[CODRhCl]_2$ (COD = 1,5-cyclooctadiene) was obtained from Strem and dried in vacuo for 24 h prior to use. Indene was obtained from Aldrich, degassed by using three repeated freeze−pump−thaw cycles, and distilled under static vacuum prior to use. Alumina (Aldrich, neutral, 150 mesh, activity Brockmann II) was degassed and dehydrated in vacuo for 48 h at temperatures between 200 and 300 °C and subsequently deactivated with 2% deionized water under argon prior to use. 2-(Dimethylamino)indene (**1**) was prepared by using literature procedures[15] and was dried in vacuo for 24 h prior to use. Compounds **2a** and **3** were also prepared using literature procedures.[4] All NMR data were collected at ambient temperature on a Bruker AC-250 spectrometer at 250.1, 62.9, and 101.3 MHz, for ^1H, ^{13}C, and ^{31}P, respectively, with chemical shifts reported in parts per million downfield of tetramethylsilane (for ^1H and ^{13}C) or 85% H_3PO_4 in water (for ^{31}P). In some cases, slightly fewer than expected independent ^{13}C NMR resonances were observed, despite prolonged data acquisition times. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Preparation of 1-(Diphenylphosphino)-2-(dimethylamino)indene (2c). Compound **2c** was prepared on the basis of the literature preparation of **2a**.[4] In a Schlenk flask containing a magnetic stir bar were added 2-(dimethylamino)-indene (0.66 g, 4.17 mmol) and THF (20 mL). The flask was then sealed with a septum and cooled to −80 °C. Magnetic stirring was initiated, and a hexanes solution of *n*-BuLi (2.6 mL of a 1.6 M solution, 4.2 mmol) was added dropwise over 3 min via syringe, after which the reaction mixture was warmed to room temperature over 3 h. Subsequently, the reaction flask was again cooled to −80 °C and chlorodiphenylphosphine (0.75 mL, 4.17 mmol) was added via syringe over 2 min. The resulting clear tan solution was warmed to room temperature and was stirred for 15 h. The THF and other volatile materials were then removed in vacuo, and the residue was washed with diethyl ether (15 mL) and dried in vacuo, leaving a cream-colored solid. Treatment of this solid with toluene (15 mL) generated a pale yellow solution, which was transferred away from the remaining insoluble materials via cannula filtration. Removal of the toluene and any other volatile materials in vacuo yielded **2c** (0.86 g, 2.52 mmol, 61%). Anal. Calcd for $C_{23}H_{22}NP$: C, 80.44; H, 6.46; N, 4.08. Found: C, 80.51; H, 6.60; N, 3.99. ^1H NMR (C_6D_6): δ 7.42−7.37 (m, 2H, Ar−H's), 7.22−6.92 (m, 10H, Ar−H's), 6.71−6.69 (m, 2H, Ar−H's), 5.13 (s, 1H, C3−H), 4.26 (d, $^2J_{PH}$ = 5.2 Hz, 1H, C1−H), 2.56 (s, 6H, N*Me*$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 148.1 (d, J_{PC} = 4.8 Hz, sp^2 *C*), 136.5 (sp^2 *C*), 128.8 (sp^2 *C*), 125.6 (d, J_{PC} = 23.4 Hz, sp^2 *C*), 122.2 (d, J_{PC} = 16.2 Hz, sp^2 *C*), 119.8 (sp^2 *C*), 118.3 (d, J_{PC} = 4.3 Hz, sp^2 *C*), 117.8−117.4 (sp^2 *C*'s), 116.9 (sp^2 *C*), 112.8 (sp^2 *C*), 110.3 (sp^2 *C*), 107.8 (sp^2 *C*), 91.4 (sp^2 *C*), 38.1 (d, J_{PC} = 29.1 Hz, C1), 31.3 (d, J_{PC} = 4.3 Hz, N(*C*H$_3$)$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 8.1.

Preparation of 1-(Diisopropylphosphino)indene (6a). In a Schlenk flask containing a magnetic stir bar were added indene (1.0 mL, 8.6 mmol) and diethyl ether (30 mL). The reaction flask was sealed with a septum, and the mixture was cooled to −80 °C. Magnetic stirring was initiated, and a hexanes solution of *n*-BuLi (5.4 mL of a 1.6 M solution, 8.6 mmol) was added dropwise over 5 min via syringe, after which the reaction mixture was warmed to room temperature over 15 h. The clear yellow solution was subsequently cooled to −80 °C, and $^{i}Pr_2PCl$ (1.4 mL, 8.6 mmol) was added via syringe over 3 min. Immediately, a cream-colored precipitate formed from the yellow-brown reaction mixture. After 20 min, magnetic stirring was arrested and the reaction mixture warmed to room temperature over 5 h. The pale yellow solution was then transferred away from the precipitated solid via cannula filtration and subsequently dried in vacuo to remove solvent and any other volatile materials, yielding **6a** as a pale yellow oil (1.85 g, 7.97 mmol, 92%). Since compound **6a** slowly rearranges to **6b** on standing, only elemental analysis data for **6b** are provided (vide infra). ^1H NMR (C_6D_6): δ 7.69 (d, $^3J_{HH}$ = 7.0 Hz, 1H, C4−H or C7−H), 7.30−7.05 (m, 3H, C5−H, C6−H, and either C7−H or C4−H), 6.71 (m, 1H, C2−H or C3−H), 6.48 (m, 1H, C3−H or C2−H), 3.71 (m, 1H, C1−H), 1.76 (m, 1H, P(C*H*Me$_2$)), 1.46 (m, 1H, P(C*H*Me$_2$)), 1.03−0.98 (m, 6H, P(CH*Me*$_2$)), 0.78 (d of d, $^2J_{PH}$ = 11.9 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*$_2$)), 0.58 (d of d, $^2J_{PH}$ = 14.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CH*Me*$_2$)). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 147.2 (d, J_{PC} = 8.6 Hz, C3a or C7a), 144.6 (d, J_{PC} = 1.9 Hz, C7a or C3a), 137.1 (sp^2 *C*−H), 131.2 (sp^2 *C*−H), 126.8 (sp^2 *C*−H), 125.3 (sp^2 *C*−H), 124.7 (d, J_{PC} = 7.6 Hz, sp^2 *C*−H), 121.9 (sp^2 *C*−H), 47.0 (d, $^1J_{PC}$ = 28.6 Hz, C1), 23.5 (d, $^1J_{PC}$ = 17.6 Hz, P(*C*HMe$_2$)), 22.6 (d, $^1J_{PC}$ = 18.6 Hz, P(*C*HMe$_2$)), 21.6 (d, $^2J_{PC}$ = 4.8 Hz, P(CH*Me*$_2$)), 21.3 (d, $^2J_{PC}$ = 5.3 Hz, P(CH*Me*$_2$)), 20.9 (d, $^2J_{PC}$ = 12.9 Hz, P(CH*Me*$_2$)), 20.7 (d, $^2J_{PC}$ = 9.5 Hz, P(CH*Me*$_2$)). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 17.3.

Preparation of 3-(Diisopropylphosphino)indene (6b). Within the glovebox, a freshly prepared solution of **6a** (1.99 g, 8.60 mmol) in diethyl ether (30 mL) was passed down an alumina column (2 cm × 4 cm). The eluted yellow solution was dried in vacuo to remove the solvent and any other volatile materials, yielding **6b** as a yellow oil (1.52 g, 6.53 mmol, 76%). Anal. Calcd for $C_{15}H_{21}P$: C, 77.56; H, 9.11. Found: C, 77.54; H, 9.08. ^1H NMR (C_6D_6): δ 7.82 (d, $^3J_{HH}$ = 7.6 Hz, 1H, C7−H or C4−H), 7.29−7.07 (m, 3H; C5−H, C6−H, and either C4−H or C7−H), 6.42 (m, 1H, C2−H), 3.10 (s, 2H, C*H*$_2$), 2.01 (d of septets, $^2J_{PH}$ = 2.1 Hz, $^3J_{HH}$ = 6.9 Hz, 2H, P(C*H*Me$_2$)$_2$), 1.08 (d of d, $^2J_{PH}$ = 14.7 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CH*Me*$_a$Me$_b$)$_2$), 0.99 (d of d, $^2J_{PH}$ = 11.9 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHMe$_a$*Me*$_b$)$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 148.7 (d, J_{PC} = 18.6 Hz, quaternary), 144.6 (d, J_{PC} = 3.8 Hz, quaternary), 141.8 (d, J_{PC} = 5.7 Hz, sp^2 *C*−H), 140.5 (d, J_{PC} = 23.4 Hz, quaternary), 126.9 (sp^2 *C*−H), 125.5 (sp^2 *C*−H), 124.3 (sp^2 *C*−H), 122.3 (d, J_{PC} = 6.7 Hz, sp^2 *C*−H), 40.3 (d, $^3J_{PC}$ = 3.8 Hz, *C*H$_2$), 23.3 (d, J_{PC} = 11 Hz, P(CH*Me*$_2$)), 21.0 (d, J_{PC} = 17.6 Hz, P(*C*HMe$_2$)), 19.9 (d, J_{PC} = 10.0 Hz, P(CH*Me*$_2$)). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −10.2.

(14) Szafran, Z.; Pike, R. M.; Singh, M. M. *Microscale Inorganic Chemistry*; Wiley: Toronto, 1991.

(15) (a) Klosin, J.; Kruper, W. J., Jr.; Nickias, P. N.; Roof, G. R.; De Waele, P.; Abboud, K. A. *Organometallics* **2001**, *20*, 2663. (b) Edlund, U.; Bergson, G. *Acta Chem. Scand.* **1971**, *25*, 3625.

Preparation of [RhCl(η^4-1,5-cyclooctadiene)(κ^1-3-^{i}Pr$_2$P-indene)] (7). In a glass vial charged with a magnetic stir bar, **6b** (0.038 g, 0.16 mmol) was dissolved in toluene (3 mL). In a separate glass vial, $[CODRhCl]_2$ (0.040 g, 0.08 mmol) was slurried in toluene (2 mL) and transferred via Pasteur pipet to the stirred solution of **6b**, resulting in a clear yellow-orange solution. The reaction vial was then sealed with a PTFE-lined cap. After 10 min, a yellow solid formed. The reaction mixture was then stirred for an additional 1.5 h, after which the supernatant was transferred away from the precipitated yellow solid via Pasteur pipet. By slightly concentrating the supernatant in vacuo, a further yellow solid precipitated, which was isolated and combined with the original solid fraction. The combined solids were then dried in vacuo to remove the remaining solvent and any other volatile materials, yielding **7 (**0.062 g, 0.13 mmol, 79%). Anal. Calcd for $C_{23}H_{33}PClRh$: C, 57.69; H, 6.95. Found: C, 57.45; H, 7.00. ^{1}H NMR (C_6D_6): δ 8.34 (d, $^3J_{HH}$ = 7.6 Hz, 1H, C7−H or C4−H), 7.27−7.08 (m, 3H, C5−H, C6−H, and either C4−H or C7−H), 6.16 (m, 1H, C2−H), 5.77 (s, 2H, vinyl-C*H*'s), 3.46 (s, 2H, vinyl-C*H*'s), 2.96 (s, 2H, C1−H's), 2.58 (m, 2H, P(C*H*Me$_a$Me$_b$)$_2$), 2.10 (d, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2CH$_2$), 1.56−1.68 (m, 4H, CH_2CH_2), 1.49 (d of d, $^3J_{PH}$ = 15.8 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CH*Me*$_a$Me$_b$)$_2$), 1.34 (m, 2H, CH$_2$CH_2), 1.06 (d of d, $^3J_{PH}$ = 13.7 Hz, $^3J_{HH}$ = 6.7 Hz, 6H, P(CHMe$_a$*Me*$_b$)$_2$). ^{13}C{^{1}H} NMR (C_6D_6): δ 142.9 (sp^2 *C*−H), 126.3 (sp^2 *C*−H), 125.9 (sp^2 *C*−H), 125.2 (sp^2 *C*−H), 124.2 (sp^2 *C*−H), 103.9 (d of d, $^1J_{RhC}$ = 12.4 Hz, $^2J_{PC}$ = 7.2 Hz, COD vinyl *C*'s), 71.0 (d, $^1J_{RhC}$ = 13.3 Hz, COD vinyl *C*'s), 40.2 (d, $^3J_{PC}$ = 6.7 Hz, C1), 33.5 (d, J_{PC} = 2.9 Hz, P(CH*Me*$_2$)), 24.5 (d, J_{PC} = 23.8 Hz, P(*C*HMe$_2$)), 21.1 (d, J_{PC} = 3.8 Hz, P(CH*Me*$_2$)), 29.1 (s, COD *C*H$_2$), 19.5 (s, COD *C*H$_2$). ^{31}P{^{1}H} NMR (C_6D_6): δ 25.7 (d, $^1J_{RhP}$ = 152 Hz).

Preparation of [Rh(η^4-1,5-cyclooctadiene)(η^5-2-Me$_2$N-C$_9$H$_6$)] (8). In a Schlenk flask containing a magnetic stir bar were added **1** (0.11 g, 0.67 mmol) and diethyl ether (10 mL), producing a light tan solution. The flask was then sealed with a septum and cooled to 0 °C. A hexanes solution of *n*-BuLi (0.42 mL of a 1.6 M solution, 0.67 mmol) was added to the stirred solution over 5 min. The reaction flask was then warmed to room temperature over 2 h, during which time a white solid precipitated. The flask was transferred to the glovebox, and a slurry of $[CODRhCl]_2$ (0.17 g, 0.34 mmol) in diethyl ether (4 mL) was added via Pasteur pipet. Immediately, a dark brown-red solution formed, along with what appeared to be a fresh white precipitate. The reaction mixture was stirred for 1 h followed by filtration through Celite. Fine brown fibers of **7** readily precipitated from the solution, which were isolated by transferring the supernatant away with a Pasteur pipet and drying in vacuo to remove any remaining solvent and other volatile materials (0.13 g, 0.36 mmol, 53%). Anal. Calcd for $C_{19}H_{24}NRh$: C, 61.79; H, 6.55; N, 3.79, found: C, 60.43; H, 6.50; N, 3.61. Repeat analyses consistently yielded low % C values. ^{1}H NMR ($CDCl_3$): δ 7.30−7.21 (m, 4H, C4−H, C5−H, C6−H, and C7−H), 5.05 (s, 2H, C1−H and C3−H), 4.29 (s, 4H, vinyl C*H*'s), 2.97 (s, 6H, N(CH_3)$_2$), 2.18−1.97 (m, 8H, (CH_2CH_2CHCH)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 121.6 (C4 and C7 or C5 and C6), 118.0 (C5 and C6 or C4 and C7), 67.7 (d, $^1J_{RhC}$ = 13.3 Hz, vinyl C's), 64.8 (d, J_{RhC} = 4.8 Hz, C1 and C3), 42.7 (N(*C*H$_3$)$_2$), 31.8 ((*C*H$_2$CH$_2$CHCH)$_2$).

Preparation of [Rh(η^4-1,5-cyclooctadiene)(η^5-1-^{i}Pr$_2$P-C$_9$H$_6$)] (9). Within the glovebox, a hexanes solution of *n*-BuLi (0.10 mL of a 1.6 M solution, 0.16 mmol) was added to a stirred solution of **6b** (0.037 g, 0.16 mmol) in diethyl ether (2 mL), and the vial was sealed with a PFTE-lined cap. A ^{31}P NMR spectrum taken of this yellow reaction solution revealed the presence of **6-Li** as the only phosphorus-containing product.[16] After 2 h, a slurry of $[CODRhCl]_2$ (0.040 g, 0.08 mmol) in diethyl ether (2 mL) was added to the reaction mixture via Pasteur pipet, whereupon the solution turned dark orange with the formation of a precipitate. After it was stirred for 16 h, the reaction mixture was filtered through Celite. ^{31}P NMR analysis of the clear brown-green filtrate revealed the presence of a single new phosphorus-containing product. Solvent and other volatile materials were then removed in vacuo, the resulting dark green greasy solid was washed once with pentane (1 mL), and the product (**9**) was dried in vacuo (0.064 g, 0.14 mmol, 88%). Anal. Calcd for $C_{23}H_{32}PRh$: C, 62.45; H, 7.29. Found: C, 62.12; H, 7.27. ^{1}H NMR (C_6D_6): δ 7.45 (d, $^3J_{HH}$ = 7.6 Hz, 1H, C4−H or C7−H), 7.28 (d, $^3J_{HH}$ = 7.6 Hz, 1H, C7−H or C4−H), 7.08−6.96 (m, 2H, C5−H and C6−H), 5.77 (m, 1H, C2−H or C3−H), 4.77 (d, J = 2.4 Hz, 1H, C3−H or C2−H), 3.98 (m, 2H, vinyl C*H*'s), 3.75 (m, 2H, vinyl C*H*'s), 2.23 (m, 1H, P(C*H*Me$_2$)), 2.12−1.27 (m, 12H, P(C*HMe*Me) and (CH_2CH_2CHCH)$_2$), 1.15 (d of d, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 12.8 Hz, 3H, P(CH*Me*Me)), 1.03 (d of d, $^3J_{HH}$ = 7.3 Hz, $^3J_{PH}$ = 13.1 Hz, 3H, P(CH*Me*Me)), 0.90 (d of d, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 10.1 Hz, 3H, P(CH*Me*Me)). ^{13}C{^{1}H} NMR (C_6D_6): δ 123.6 (sp^2 *C*−H), 122.2 (sp^2 *C*−H), 121.1 (sp^2 *C*−H), 120.3 (d, J = 5.7 Hz, sp^2 *C*−H), 96.3 (t, J = 4.3 Hz, sp^2 *C*−H), 76.5 (d, J = 4.3 Hz, sp^2 *C*−H), 70.6 (d, J_{RhC} = 13.8 Hz, vinyl *C*H's), 70.0 (d of d, J_{PC} = 4.3 Hz, J_{RhC} = 13.8 Hz, vinyl *C*H's), 32.2 ((*C*H$_2$CH$_2$CHCH)$_2$), 31.5 ((CH$_2$*C*H$_2$CHCH)$_2$), 25.9 (d, $^1J_{PC}$ = 16.2 Hz, P(*C*HMe$_2$)), 23.0 (d, $^1J_{PC}$ = 17.6 Hz, P(*C*HMe$_2$)), 22.9 (d, $^2J_{PC}$ = 11.4 Hz, P(CH*Me*$_2$)), 21.1 (d, $^2J_{PC}$ = 9.5 Hz, P(CH*Me*$_2$)), 20.9 (d, $^2J_{PC}$ = 11.4 Hz, P(CH*Me*$_2$)), 19.5 (d, $^2J_{PC}$ = 7.2 Hz, P(CH*Me*$_2$)). ^{31}P-{^{1}H} NMR (C_6D_6): δ −11.8.

Formation of 10. In a Schlenk flask equipped with a magnetic stir bar, **6b** (0.12 g, 0.54 mmol) was dissolved in diethyl ether (10 mL) within the glovebox. The reaction flask was sealed with a septum and transferred to the Schlenk line. The flask was then cooled to 0 °C, and magnetic stirring was initiated. A hexanes solution of *n*-BuLi (0.86 mL of a 1.6 M solution, 1.4 mmol) was subsequently added to the flask over 2 min via syringe, and the yellow solution was then stirred for 2 h as it warmed to room temperature. A ^{31}P NMR spectrum taken of an aliquot of this yellow solution confirmed the clean formation of **6-Li**. The reaction flask was then taken back into the glovebox, and a slurry of $[CODRhCl]_2$ (0.13 g, 0.26 mmol) in toluene (4 mL) was added via Pasteur pipet. Immediately, the reaction mixture turned dark red-brown and a lightly colored precipitate formed. After 1 h, ^{31}P NMR analysis of the reaction solution revealed the formation of **9** (δ −11.8) as the major product. The reaction mixture was then concentrated in vacuo and filtered through Celite into a glass vial. The vial was then sealed with a PFTE-lined cap and stored at −30 °C. Initially, no crystalline material was produced. However, after 3 months a minute quantity of red crystals was isolated by transferring the supernatant away via Pasteur pipet into a separate glass vial. Single-crystal X-ray analysis of the isolated crystals revealed their identity to be **10**. A subsequent ^{31}P NMR analysis of the supernatant from which the crystals had grown revealed a sharp singlet at δ −11.8 (attributable to **9**) but also many new rhodium-coupled products in the range δ 75.9−48.9. Satisfactory NMR data for the isolated crystals of **10** could not be obtained, and no further material was isolated from this reaction mixture in pure form.

Isomerization of 1-(Diisopropylphosphino)-2-(dimethylamino)indene (2a). Within the glovebox, a 0.02 g sample of **2a** was dissolved in C_6D_6 (2 mL) in a glass vial equipped with a magnetic stir bar. The initial ^{31}P NMR spectrum of this solution revealed only one signal at 19.6 ppm. To this solution was added alumina (2 g), and the vial was subsequently sealed with a PTFE-lined cap. After the mixture was stirred for 2 h, a ^{31}P NMR spectrum was obtained of the resulting yellow solution, which revealed two resonances at chemical shifts of 19.6 ppm (**2a**) and −2.9 ppm (tentatively assigned as **2b**) in

(16) We have found lithium salts of phosphinoindenes to be rather unstable in the solid state. As such, the preparation of **6-Li** is carried out in situ by treating a solution of **6b** with *n*-BuLi. We attribute the single phosphorus resonance in the ^{31}P NMR spectrum (δ −8.9) of the resulting solution to **6-Li**.

an approximate ratio of 3:1. The mixture was stirred for 2 weeks with periodic monitoring by using ^{31}P NMR spectroscopy; no further changes in the peak ratios were observed.

Isomerization of 1-(Diphenylphosphino)-2-(dimethylamino)indene (2c). Using a protocol analogous to that described for the isomerization of **2a**, a freshly prepared sample of **2c** (0.02 g) dissolved in C_6D_6 (2 mL) was stirred over alumina (2 g). After 2 h, a ^{31}P NMR spectrum obtained from an aliquot of the reaction mixture revealed two resonances at chemical shifts of 8.1 ppm (**2c**) and −24.8 ppm (**2d**) in an approximate ratio of 1:3. The mixture was stirred for 72 h with periodic monitoring by using ^{31}P NMR spectroscopy; no further changes in the peak ratios were observed. ^{1}H NMR (C_6D_6) for **2d**: δ 7.74−7.71 (m, 2H, Ar H's), 7.21−6.91 (m, 10H, Ar H's), 6.87−6.83 (m, 2H, Ar H's), 3.09 (s, 2H, CH_2), 2.71 (s, 6H, NMe_2).

X-ray Crystallography. Single-crystal samples of **2d** and **3**·C_6H_6 were obtained from hexanes and benzene, respectively, by slow solvent evaporation; crystalline samples of **7** and **10**·C_7H_8 were grown from toluene and toluene/diethyl ether (1:1), respectively, at −30 °C. X-ray crystallographic data for **2d**, **3**·C_6H_6, **7**, and **10**·C_7H_8 were collected on a Bruker PLATFORM/SMART 1000 CCD instrument at 193(2) K, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Programs for diffractometer operation, data collection, data reduction, and absorption correction were those supplied by Bruker. Structural refinement was carried out by using full-matrix least-squares methods on F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added at calculated positions and refined using a riding model. Complete details are provided in the Supporting Information.

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Supporting Information Available: Tables giving single-crystal X-ray diffraction data for **2d**, **3**·C_6H_6, **7**, and **10**·C_7H_8; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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