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Synthesis and Ruthenium Coordination Complexes of the Chelating Phosphine Phosphonium-1-indenylide 1,1-Bis(diphenylphosphino)methane-1-indenylide,1-$C_9H_6Ph_2PCH_2PPh_2$

Riaz Hussain, Kevin G. Fowler, Francoise Sauriol, and Michael C. Baird*

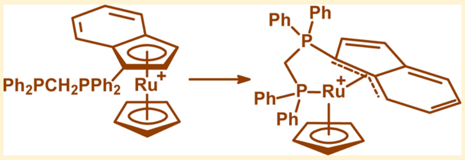
Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6, Canada

Peter H. M. Budzelaar*

Department of Chemistry, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

Ⓢ *Supporting Information*

ABSTRACT: Bis(diphenylphosphino)methane-1-indenylide, 1-$C_9H_6PPh_2CH_2PPh_2$ (1-C_9H_6dppm, **I**), has been synthesized and characterized by NMR spectroscopy and X-ray crystallography. **I** reacts with $[CpRu(MeCN)_3]PF_6$ to form the conventional sandwich complex $[CpRu(\eta^5\text{-}\mathbf{I})]PF_6$ (**II**), which contains a dangling $-PPh_2$ group. Complex **II** isomerizes to the 18-electron species **IIIc**, in which the dangling $-PPh_2$ group coordinates to the ruthenium, forcing slippage of the five-membered ring to an unanticipated 1,9,8-η^3-exo mode of coordination.



Triphenylphosphonium cyclopentadienylide, $C_5H_4PPh_3$, has been known since 1956,[1] when its unusual stability was noted and attributed to the electron delocalization implied by the zwitterionic resonance structure **b** of Figure 1.

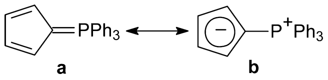


Figure 1. Resonance structures **a** and **b** of $C_5H_4PPh_3$.

Phosphonium cyclopentadienylides of this type are thus isoelectronic with neutral arene and anionic cyclopentadienyl ligands, although, as has been noted, the coordination chemistry of this class of very interesting ligands has received little systematic attention in spite of its clear potential.[2−4a] In an effort to expand the coordination chemistry of the phosphonium cyclopentadienylides, we earlier carried out an investigation of transition-metal complexes of phosphonium cyclopentadienylides and reported the synthesis and reactivity of the group 6 compounds $M(\eta^5\text{-}C_5H_4PMePh_2)(CO)_3$ (M = Cr, Mo, W) of the ligand $C_5H_4PMePh_2$, methyldiphenylphosphonium cyclopentadienylide.[2,3] We found, inter alia, that the donor properties of $C_5H_4PMePh_2$ fall between those of benzene and the cyclopentadienyl (Cp) ligand, consistent with the presence of a partial negative charge on the five-membered ring and suggesting that there would be interesting comparisons and contrasts to be made with the chemistry of similar arene and cyclopentadienyl complexes.

In order to broaden the chemistry of this general class of ligand, we subsequently began an investigation of the phosphonium-1-indenylide (PHIN) ligands 1-$C_9H_6PR_3$ (Figure 2).[5] The first such compound, triphenylphosphonium-1-indenylide, was reported in the 1960s, although it was not characterized by NMR spectroscopy or crystallography.[6a] In 2004 two PHIN analogues, 1-$C_9H_6P(CH_2Ph)Ph_2$ and 1-$C_9H_6P(CH_2C_6F_5)Ph_2$, were reported and characterized.[6b]

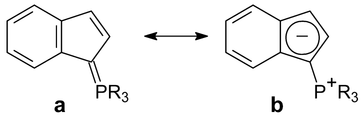


Figure 2. Resonance structures of phosphonium-1-indenylides.

Adding to their interest, PHIN ligands are planar prochiral, with the result that their coordination compounds exhibit planar chirality (Figure 3). Thus, as an example, we reported the synthesis and characterization, including crystallographic, of the planar chiral chromium compound $Cr(\eta^5\text{-}1\text{-}C_9H_6PMePh_2)(CO)_3$.[5] On the basis of the IR spectrum in the carbonyl region, the indenylide ligand was found to exhibit donor properties very similar to those of its cyclopentadienylide analogue.[5]

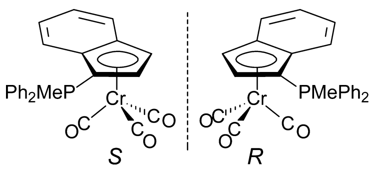


Figure 3. Enantiomers of the chiral complex $Cr(\eta^5\text{-}1\text{-}C_9H_6PMePh_2)(CO)_3$.

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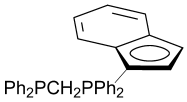
More recently we reported new and/or improved syntheses of the PHIN ligands triphenylphosphonium-1-indenylide (1-$C_9H_6PPh_3$), methyldiphenylphosphonium-1-indenylide (1-$C_9H_6PMePh_2$), and dimethylphenylphosphonium-1-indenylide (1-$C_9H_6PMe_2Ph$), as well as syntheses of the corresponding planar chiral ruthenium(II) complexes $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}1\text{-}C_9H_6PPh_3)]PF_6$, $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}1\text{-}C_5H_4PMePh_2)]PF_6$, and $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}1\text{-}C_9H_6PMe_2Ph)]PF_6$.[7] The ruthenium complexes were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, by X-ray crystallography, and by extensive DFT calculations, which provided insights into the nature of the metal−ligand bonding. The PHIN−Ru bond strengths were calculated to be ∼20 kcal/mol greater than the corresponding benzene−Ru bond strength of $[Ru(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]^+$, compatible with the observed configurational stability of the chiral complexes.

We have now extended the scope of PHIN ligands to an example involving a diphosphine and report here the synthesis and characterization of the potentially chelating phosphonium-1-indenylide bis(1,1-diphenylphosphino)methane-1-indenylide, 1-C_9H_6dppm (**I**), containing a dangling $-PPh_2$ tertiary phosphine moiety.



I

The coordination chemistry of this ligand is explored, and we have characterized the sandwich complex $[Ru(\eta^5\text{-}C_5H_5)(\eta^5\text{-}1\text{-}C_9H_6dppm)]PF_6$ (**II**), which isomerizes to a species which appears to be the unprecedented chelate complex $[CpRu(1,9,8\text{-}\eta^3\text{-}1\text{-}C_9H_6PPh_2CH_2\text{-}\kappa PPh_2]PF_6$ (**IIIc**).

RESULTS AND DISCUSSION

We previously prepared PHIN ligands by reaction of the appropriate phosphine with 1-bromoindene to form the corresponding phosphonium salt as mixtures of regioisomers; these, on deprotonation with NaH in THF, afforded the corresponding PHIN ligands.[7] We have accordingly found that reaction of 1-bromoindene with dppm in a 1:1 ratio gives in good yield the expected phosphonium salt, (1-C_9H_7dppm)Br, as a mixture of regioisomers **A** and **B**, as indicated in Figure 4.

The ^{31}P NMR spectrum of the mixture exhibited two pairs of doublets, those at δ 30.4 and −25.6 (J_{PP} = 62.0 Hz) being assigned on the basis of 1D and 2D NMR experiments as the resonances of isomer **A** and those at δ 14.4 and −25.5 (J_{PP} = 63.6 Hz) as resonances of isomer **B**. The resonances with negative chemical shifts are assigned to the dangling $-PPh_2$ groups on the basis of their very close similarity and their similarity to the ^{31}P chemical shift of free dppm (δ −23.6).

The ^1H NMR spectrum of the product mixture was complex because of the presence of the two regioisomers and was not fully interpreted. However, since isomer **A** contains a chiral center at C(1), the P−CH_2−P hydrogens are diastereotopic and distinct one-hydrogen triplet resonances could be readily identified at δ 4.53 and 4.94 ($J_{HH} \approx J_{HP} \approx$ 14.6 Hz for both). In contrast, the corresponding two-hydrogen resonance of isomer **B** was reasonably assigned to a doublet at δ 4.49 ($J_{HP} \approx$ 14.4 Hz).

Interestingly, a $^1H-^{31}P$ HMBC spectrum of a mixture showed that both methylene protons in isomer **A** couple to the phosphonium resonance at δ 30.4 and not to the resonance of the dangling $-PPh_2$ group at δ −25.6. Similarly, the methylene protons in isomer **B** couple strongly to the phosphonium resonance at δ 14.4 and relatively weakly to the resonance of the dangling $-PPh_2$ at δ −25.5. The reasons for the great differences in values of $^2J_{HP}$ are attributed to differences in the s character of the two types of P−CH_2 bonds in isomers **A** and **B**. It is well-known that values of J_{HP} of trigonal phosphines (essentially p^3 bonding) are generally much lower than corresponding values of J_{HP} of analogous tetrahedral phosphonium compounds (sp^3 bonding),[8a−c] and the same correlation appears to apply here also.

X-ray-quality crystals of isomer **A** were obtained by layering a CH_2Cl_2 solution with hexanes, and the structure is shown in Figure 5. Full crystallographic information is given in the Supporting Information, and we note here only that the chirality at C(1) and the presence of the C(2)−C(3) C═C double bond (1.335(3) Å) are confirmed.

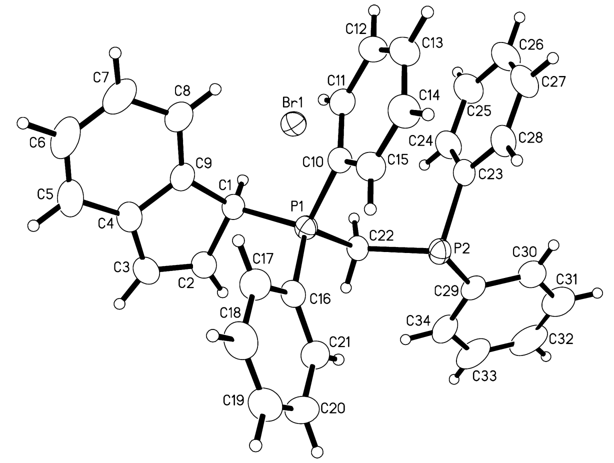


Figure 5. X-ray structure of isomer **A** of (1-C_9H_7dppm)Br.

Deprotonation of (1-C_9H_7dppm)Br with NaH in THF afforded the green, air-sensitive PHIN ligand 1-C_9H_6dppm (**I**). ^1H and ^{13}C NMR assignments can be found in Table 1 and

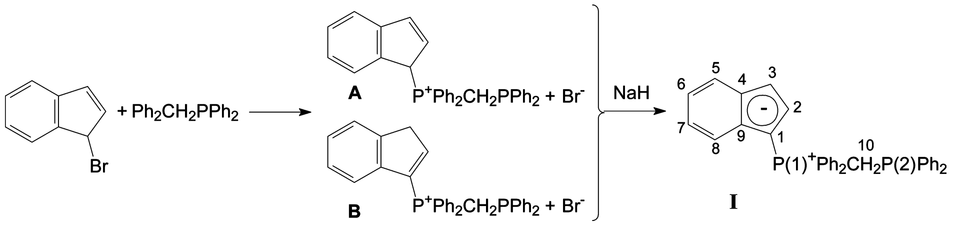


Figure 4. Synthetic route to **I**. Also indicated is the numbering scheme utilized henceforth for spectroscopic and crystallographic purposes.

Table 1. ^{1}H and ^{13}C NMR Data for I−IV

	I		II		III		IV
H, C Position	δ(^{1}H); J (Hz)	δ(^{13}C); J (Hz)	δ(^{1}H); J (Hz)	δ(^{13}C); J (Hz)	δ(^{1}H); J (Hz)	δ(^{13}C); J (Hz)	δ(^{1}H)
1		66.7 (dd, J_{CP} 2.3, 120.1)		59.6 (d, J_{CP} 102.5)		46.4 (d, J_{CP} 81.5)	
2	6.91 (t, J_{HH}, J_{HP} 4.8)	126.8 (d, J_{CP} ~14)	4.96 (t, J_{HH} 2.5, J_{HP} 2.5)	78.8 (dd, J_{CP} 13.7, 6.9)	7.63 (s)	142.1 (d, J_{CP} 8.7)	NA[a]
3	6.57 (t, J_{HH}, J_{HP} 4.8)	107.0 (d, J_{CP} 15.4)	5.79 (t, J_{HH} 2.5, J_{HP} 2.5)	71.9 (d, J_{CP} 9.3)	7.17 (s)	123.6 (d, J_{CP} 10.7)	6.46
4		138.3 (d, J_{CP} 15.8)		95.2 (d, J_{CP} 12.0)		148.3 (d, J_{CP} 6.5)	
5	7.59 (m)	120.6 (s)	7.54 (m)	126.7 (s)	7.84 (m)	122.8 (s)	6.96
6	6.87 (t, J_{HH} 7.4)	117.3 (s)	7.03 (ddd, J_{HH} 8.7, 6.5, 0.8)	126.0 (s)	7.49 (m)	125.2 (s)	6.64
7	6.70 (t, J_{HH} 7.4)	117.9 (s)	6.87 (ddd, J_{HH} 8.9, 6.4, 1.2)	125.8 (s)	7.60 (m)	129.0 (s)	6.21
8	6.90 (m)	117.8 (s)	6.75 (dd, J_{HH} 8.9, 0.6)	124.4 (d, J_{CP} 9.4)	4.45 (dd, J_{HH} 6.4 $J_{HP(2)}$ 10.5)	70.4 (s)	6.50
9		135.9 (d, J_{CP} 14.1)		97.4 (d, J_{CP} 10.0)		98.0 (d, J_{CP} 6.3)	
PCH$_2$P	3.73 (d, J_{HP} 13.5)	27.2 (dd, J_{CP} 57.4, 35.4)	3.83 (m, J_{HH} 15.0, J_{HP} ~14) 3.87 (m, J_{HH} 15.0, J_{HP} ~14)	27.5 (dd, J_{CP} 36.9, 27.3)	2.81 (dt, J_{HH} 16.25 J_{HP} 6.9), 4.10 (dt, J_{HH} 16.15, J_{HP} 9.3	30.6 (dd, J_{CP} 70.2, 7.6)	2.81, 4.10
Ph	7.20−7.75 (m)	128−136	7.30−7.83	125−135	see Figure 7	125−135	
C$_5$H$_5$			4.34 (s)	73.8 (s)	3.58 (s)	80.0 (s)	4.16

[a] NA = not assigned.

correspond well with values observed for previously reported PHIN ligands.[7] The ^{31}P NMR spectrum exhibited doublet resonances, at δ 7.5 and −28.3 (J_{PP} = 61 Hz); these are assigned to the ylidic and phosphine phosphorus atoms, respectively, on the basis of comparisons with data for previously reported PHIN ligands[7] and free dppm (δ −23.6). Of note, as with the isomeric phosphonium cations, the two $^2J_{HP}$ values for the P−CH$_2$ group were quite different: 13.5 Hz to the ylidic phosphorus and ~0 Hz for the phosphine phosphorus atom.

X-ray-quality crystals of **I** were obtained by layering a CH$_2$Cl$_2$ solution with hexanes, and the structure is shown in Figure 6.

The bond lengths of **I** are very similar to the corresponding bond lengths of 1-C$_9$H$_6$PPh$_3$, 1-C$_9$H$_6$PMePh$_2$, and 1-C$_9$H$_6$PMe$_2$Ph.[7] Thus, for instance the P(1)−C(1) bond length of **I** is 1.715(3) Å in comparison with an average of 1.72 Å for the other PHIN ligands and is shorter than the P(1)−CH$_2$ and P(2)−CH$_2$ bond distances, 1.812(2) and 1.859(2) Å, respectively, and the average of the P−Ph distances, 1.82 Å. Thus, the P−ylide bond possesses considerable double-bond character. The dimensions of the five- and six-membered rings also compare well with those of 1-C$_9$H$_6$PPh$_3$, 1-C$_9$H$_6$PMePh$_2$, and 1-C$_9$H$_6$PMe$_2$Ph,[7] with some shortening of C(2)−C(3) (1.365(4) Å), C(5)−C(6) (1.378(4) Å), and C(7)−C(8) (1.371(3) Å) relative to the other ring C−C distances (1.401(4)−1.441(3) Å). Full crystallographic information is given in the Supporting Information.

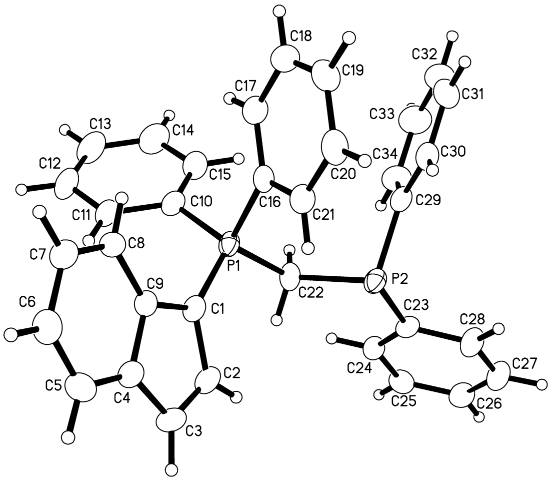
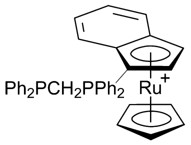


Figure 6. X-ray structure of 1-C$_9$H$_6$dppm (**I**).

Compound **I** was found to react with the labile ruthenium(II) complex [CpRu(MeCN)$_3$]PF$_6$[9] in CH$_2$Cl$_2$ to give bright red solutions containing two major products, the relative amounts of which varied with time. Reactions in CD$_2$Cl$_2$ were therefore monitored by NMR spectroscopy, with the finding that the ^{31}P NMR spectrum of the kinetic product (**II**) exhibited doublets at δ 23.0 and −29.1 (J_{PP} = 69 Hz) while that of the thermodynamic product (**III**) exhibited doublets at δ 37.7 and 58.1 (J_{PP} = 71 Hz) (see the Supporting Information, Figure S1); the conversion of **II** to **III** was complete within 10 days at room temperature. Spectra sometimes also contained resonances of a very minor product, indicated by an AB quartet at δ 21.63 and 21.24 (J_{PP} = 12.1 Hz); this will be discussed below.

By analogy with previous work which showed that reactions of [CpRu(MeCN)$_3$]PF$_6$ with other PHIN ligands under similar conditions give sandwich complexes of the type [CpRu(η^5-PHIN)]PF$_6$,[7] we anticipated that one of the products would be [CpRu(η^5-**I**)]PF$_6$ (**II**).



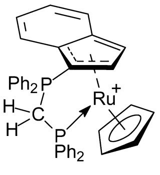
II

Such a structure contains a dangling $-PPh_2$ group, and it was therefore gratifying to note that the chemical shift of the resonance at δ −29.1 in the ^{31}P spectrum of the kinetic product is very similar to that of the dangling $-PPh_2$ in the uncoordinated PHIN-dppm ligand, δ −28.3. The resonance at δ 23.0 is therefore to be attributed to the ylide phosphorus and, by analogy with previously studied sandwich complexes of the type [CpRu(η^5-PHIN)]PF_6,[7] η^5 coordination of **I** to Ru(II) to give **II** should result in a downfield shift of the ylide ^{31}P resonance of about 14−21 ppm. This is as found (δ 23.0 vs δ 7.5; $\Delta\delta$ = 15.5 ppm), and thus the NMR data are all consistent with assignment of the kinetic product as **II**. All attempts to grow crystallographically useful crystals unfortunately failed but, as with the aforementioned complexes of monodentate PHIN ligands,[7] a freshly prepared electrospray mass spectrum (ES-MS, MeCN) exhibited solely a multiplet centered at *m*/*e* 665 with an isotopic pattern in excellent agreement with the calculated spectrum.

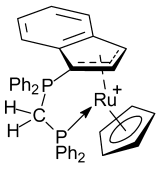
Since **II** could not be characterized crystallographically, the structure was of necessity inferred from a series of 1D and 2D NMR experiments (^{31}P, ^{1}H, ^{1}H{^{31}P}, HMBC (H−C and H−P), NOESY, COSY, HSQC). The ^{1}H NMR spectrum of a mixture of **II** and **III** (see the Supporting Information, Figure S2) is very complex and challenging to interpret since, for example, **II** and **III** both contain four nonequivalent phenyl groups and, of course, the relative amounts of the two species were continually changing. However, by monitoring relative intensities as a function of time, it was possible to identify many of the resonances of **II**, as indicated in Table 1; a number of the phenyl resonances were obscured, and therefore these are not listed. These assignments were strengthened to an extent by an H−P HMBC experiment (Figure S5, Supporting Information), which showed that the ^{31}P resonance of **II** at δ −29.1 correlates with multiplets in the ^{1}H NMR spectrum at δ 3.85, 7.30, and 7.4, while that at δ 23.0 correlates with the multiplet at δ 3.85 and with others at δ 7.55, 7.67, and 7.82. In addition, the ^{31}P resonance of **III** at δ 37.8 correlates with multiplets in the ^{1}H NMR spectrum at δ 2.81, 4.10, 7.17, 7.41, 7.65, 7.84, and 8.20, while that at δ 58.1 correlates with the multiplets at δ 2.81, 4.10, and 4.45 and with others at δ 6.98, 7.19, 7.65, and 8.09.

Readily identified on the basis of relative intensities and a lack of correlations with any other protons in a COSY spectrum of a mixture (Figure S6, Supporting Information) were the Cp and PCH_2P resonances of **II** at δ 4.34 (s) and 3.85 (m), respectively. The latter multiplet is actually composed of two doublet of doublets because the protons at position 10 are not equivalent and appear as an AB quartet in the ^{1}H{^{31}P} NMR spectrum (Figure S3, Supporting Information). The COSY spectrum also showed that the resonance at δ 4.96 correlated only with that at δ 5.79 and these were assigned to H(2) and H(3), respectively, of **II**. In confirmation of these assignments, a NOESY spectrum (Figure S7, Supporting Information) exhibited through-space interactions of the resonance at δ 5.79 with that at δ 4.96 and also with a resonance at δ 7.54, which is therefore assigned to H(5). Similar correlations allowed assignment of resonances at δ 7.03, 6.87, and 6.75 to H(6), H(7), and H(8), respectively. ^{13}C assignments for **II**, based on HSQC (Figure S8, Supporting Information) and HMBC (Figure S9, Supporting Information) experiments, can be found in Table 1. As anticipated, since **II** is similar in structure to previously studied sandwich complexes of the type [CpRu(η^5-PHIN)]PF_6,[7] the chemical shifts of the indenyl ring hydrogens of **II** are very similar to those reported previously.[7]

Interestingly, both of the ^{31}P resonances of the thermodynamic product (δ 37.7, 58.1) lie well downfield of the ^{31}P resonances of the free ligand. There are no precedents as yet for such coordination shifts for coordination complexes of PHIN ligands,[5,7] but the apparently very large downfield coordination shift from δ −28.3 of the dangling $-PPh_2$ of free **I** calls to mind previous observations of anomalously large ^{31}P downfield coordination shifts in the case of five-membered chelate rings.[10] For instance, ^{31}P chemical shifts of chelated 1,2-bis(diphenylphosphino)ethane (dppe) complexes are routinely some 20−40 ppm downfield of the corresponding chemical shifts of 1,2-bis(diphenylphosphino)propane (dppp) and 1,2-bis(diphenylphosphino)butane (dppb) complexes, although the ^{31}P chemical shifts of the free phosphines are similar.[10] It thus seemed quite likely that the thermodynamic product contains **I** chelated to the ruthenium in such a manner that a five-membered ring is formed, and we initially considered the η^3-allylic species [CpRu(2,1,9-η^3-1-$C_9H_6PPh_2CH_2$-$\kappa P$$Ph_2$]$PF_6$ (**IIIa**) and [CpRu(1,2,3-η^3-1-$C_9H_6PPh_2CH_2$-$\kappa P$$Ph_2$]$PF_6$ (**IIIb**).



IIIa



IIIb

Structures **IIIa,b** both obey the 18-electron rule and thus appear to be reasonable, although η^3-allylic structures for phosphonium cyclopentadienylides have not previously been reported. Ring slippage as in **IIIb** would, however, be analogous to the well-known indenyl effect[11] in which an η^5-indenyl complex rearranges to an η^3 mode of coordination, freeing up a coordination site and permitting associative substitution reactions of neighboring ligands. The process is made possible because of stabilization of the six-membered aromatic ring.[11]

Since **III** could not be characterized crystallographically, the structure was of necessity inferred from a series of ES-MS and NMR experiments, as with **II**, supported by DFT calculations. Experiments involved the utilization of somewhat aged samples which contained predominantly **III** (by NMR), and it was gratifying to note that the ES-MS spectrum of the product mixture exhibited the same multiplet centered at *m*/*e* 665. Thus, the kinetic and thermodynamic products were indeed isomeric.

As with **II**, the Cp (δ 3.58 (s)) and nonequivalent PCH_2P (δ 2.81 (dt), 4.10 (dt)) resonances were readily identified on the basis of relative intensities and a lack of correlations with any other protons in a COSY spectrum of a mixture (Figure S6, Supporting Information) (although, of course, the resonances at δ 2.81 and 4.10 were mutually coupled). The COSY spectrum also exhibited correlation between resonances at δ 7.17 and 7.63, neither of which exhibited correlations to other protons. As discussed above for **II**, this type of correlation is as expected for the resonances of H(2) and H(3) and it was subsequently found that NOESY correlations existed between these two resonances, between the resonance at δ 7.17 with another at δ 7.84 and between resonances at δ 4.43 and 7.60. Thus, the resonances at δ 7.63 and 7.17 are assigned to H(2) and H(3), respectively, and those at δ 7.84, 7.60 and 4.46 are assigned to H(5), H(7), and H(8), respectively. These assignments were confirmed by detailed considerations of the COSY spectrum, which also suggested that a resonance at δ 7.49 may be assigned to H(6).

Interestingly, an H−P HMBC spectrum exhibited a weak correlation between the resonance of H(3) at δ 7.17 and the phosphorus resonance at δ 37.8, and thus the latter can be assigned to the ylidic phosphorus P(1) and that at δ 58.1 to the coordinated phosphorus P(2). (A stronger correlation between P(1) and H(2) is likely, but the presumed cross-peak is obscured.)

In an attempt to obtain more information about the structure of **III**, it was noted that the ^{1}H resonances at δ 7.41, 8.20, 6.98, and 8.09 were all greatly simplified upon phosphorus decoupling (compare Figures S2−S4); it follows that these resonances are to be attributed to the ortho protons of the four *P*-phenyl rings. Further detailed considerations of the COSY and H−P HMBC spectra resulted in conclusions that the resonances at δ 7.41 and 8.20 may be attributed to the phenyl rings bonded to the ylidic phosphorus P(1) and those at δ 6.98 and 8.09 to the coordinated phosphorus P(2). Indeed, all ^{1}H chemical shifts on the four phenyl groups were ultimately determined from COSY and NOESY spectra and are shown in Figure 7.

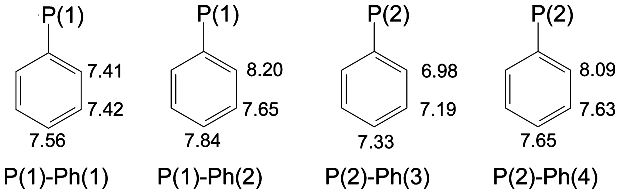


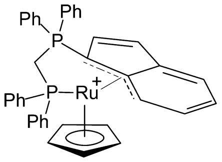
Figure 7. ^{1}H chemical shifts of the phenyl groups in **III**: Ph(1) and Ph(2) bonded to the ylidic phosphorus P(1) and Ph(3) and Ph(4) bonded to P(2).

The NOESY spectrum also provided insight into the relative orientations of the indenylide and the groups of the dppm moiety in **III**. Strong NOEs were observed between the resonance of H(8) and the CH_2 resonance at δ 2.81 (henceforth proton H(10a)), and between the Cp resonance and the CH_2 resonance at δ 4.10 (henceforth proton H(10b)). Thus, H(10b) is oriented toward the Cp ligand while H(10a) lies relatively close to H(8) and thus must point toward the six-membered ring of the indenylide ligand. *The fact that the resonance of proton H(10a) does not exhibit an NOE with the resonances of H(2) or H(3) would seem to rule out either **IIIa** or **IIIb** as the structure of the thermodynamic product.*

An NOE was also observed between the resonance of the Cp ligand and that of the *o*-H of Ph(3), as were medium NOEs between the resonance of the Cp ligand and those of the *o*-H atoms of Ph(2) and Ph(4). However, no NOE was observed between the resonance of the Cp ligand and that of the *o*-H of Ph(1), and thus the Cp ligand must be oriented toward Ph(2), Ph(3), and Ph(4) but away from Ph(1).

A series of ^{13}C, HSQC, and HMBC spectra (Figures S8 and S9, Supporting Information) were used to assign ^{13}C resonances of **III**, and the resulting chemical shifts and coupling constants can be found in Table 1. Of note are the unusual chemical shifts of C(8) (δ 70.4) and C(9) (δ 98.0), shielded by ~48 and 38 ppm, respectively, relative to the corresponding chemical shifts of the free ligand. Similar shielding has been reported previously for bound carbon atoms in η^{5}-1-indenyl complexes of ruthenium[7] and is observed here for the corresponding carbon atoms of **II**.

These observations seem most consistent with the structure of $[CpRu(1,9,8\text{-}\eta^{3}\text{-}1\text{-}C_9H_6PPh_2CH_2\text{-}\kappa PPh_2]PF_6$ (**IIIc**), in which the ruthenium center is bonded in an allylic fashion through C(1), C(9), and C(8).



IIIc

Corroborating this structure, as noted above, spin−spin coupling is observed between the P(2) resonance at δ 58.1 and the resonance of H(8) at δ 4.45, three-bond coupling which requires coordination of C(8) to the ruthenium as in **IIIc**. Rationalization of the aforementioned NOEs in terms of this structure will be presented below in the context of DFT calculations.

Interestingly, the NOESY spectrum of **IIIc** showed a significant number of cross peaks due to exchange in addition to through-space interactions. In fact, every peak assigned to **IIIc** has an exchange cross peak with an unknown compound **IV**, with the exception of the methylene protons. The peaks in the ^{1}H NMR spectrum corresponding to **IV** are too weak to be analyzed meaningfully, and the equilibrium between these species is strongly in favor of **IIIc**; however, most of the ^{1}H chemical shifts for **IV** can be assigned and are given in Table 1.

Isomerization of **IIIc** to **IV** results in shielding of all the protons on the indenylide ring, with the exception of H(8), which is deshielded considerably to a value more typical for a phenyl proton. Coordination of **I** in **IV** therefore does not involve C(8). Several of the phenyl protons also shift considerably upon isomerization; for example, the ortho proton at δ 8.10 shifts to δ 6.35. The dramatic change in chemical environment may be caused by shifting from the deshielding to the shielding zone of the Cp ring.

Finally, as noted above, synthesis of mixtures of **II** and **IIIc** sometimes resulted in the formation of a relatively minor species which exhibited an AB quartet at δ 21.63 and 21.24 (J_{PP} = 12.1 Hz) in the ^{31}P NMR spectrum. This species was not always present in reaction mixtures, and we ignored it until we happened to run a ^{31}P NMR spectrum of a sample which had aged somewhat in an NMR tube. The ^{31}P NMR spectrum of the sample was now found to exhibit, in comparable amounts, the resonances of **IIIc** *and* the AB quartet at δ 21.63, 21.24, while an ES-MS spectrum exhibited both the multiplet of **IIIc** centered at *m*/*e* 665 and a second multiplet centered at *m*/*e* 681, with an isotopic pattern in excellent agreement with that anticipated for a monoruthenium species. The difference in mass between **IIIc** and the new species corresponds to one oxygen atom, and it seems likely that the phosphine phosphorus atom had undergone slow oxidation by adventitious oxygen to give the corresponding η^{5} complex of 1-$C_9H_6PPh_2CH_2POPh_2$, containing a dangling phosphine oxide group. While assignments of neither the ^{1}H nor the ^{31}P NMR spectra have been possible, we note that the two ^{31}P chemical shifts are very similar to both that of the phosphonium ^{31}P resonance of **II**, as would be expected, and also those in the compounds $Ph_2P(O)CH_2PPh_2$ (δ 27.76)[8d] and $Ph_2P(O)CH_2P(O)Ph_2$ (δ 24.5).[8e]

Computational Results. Neither **II** nor **IIIc** could be recrystallized satisfactorily, and computational studies were therefore carried out for the η^5-1-indenyl complex **II** and for several η^3-κPPh$_2$ chelating isomers such as **IIIa–c**. Complex **II** was found to exhibit a sandwich structure very similar to those of analogous structures containing simple 1-indenylides,[7] and although the calculated Ru–C distances are slightly longer than analogous crystallographically determined Ru–C distances,[7] the metal–indenyl bonding was found to exhibit the expected three short (~2.22 Å) and two long (~2.32 Å) Ru–C bond distances. In addition, the six-membered ring of the 1-indenylide ligand exhibits short C(5)–C(6) and C(7)–C(8) bonds. As indicated above, the NMR data for **II** are also consistent with the anticipated sandwich structure, which now seems confirmed.

A number of discrete local minima, differing in which carbons of the indenyl ligand interact with the ruthenium atom, were found for the η^3-κPPh$_2$ chelate isomers but, to our initial surprise, neither **IIIa** nor **IIIb** was the lowest energy isomer. The most stable structure located is in fact essentially that discussed above as **IIIc**, albeit with the ylidic phosphorus P(1) lying well above the five-membered ring, which is essentially planar (Figure 8).

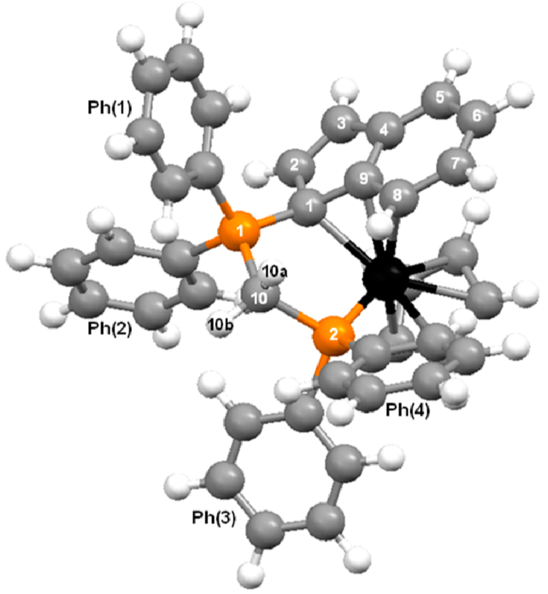


Figure 8. Computed structure of the lowest energy η^3-allylic isomer, corresponding to **IIIc**.

In this structure, the Ru–C(1), Ru–C(8), and Ru–C(9) distances are calculated to be in the range 2.27–2.55 Å, while the Ru–C(2), Ru–C(3), and Ru–C(4) distances are all calculated to be >3.2 Å and thus nonbonding. Interestingly, the C(2)–C(3), C(4)–C(5), and C(6)–C(7) distances are all relatively short, consistent with the structure shown.

The geometry of structure **IIIc** is also consistent with subtle details of the NOESY experiments discussed above. For instance, the NOESY experiment suggested strongly that H(10a) lies close to H(8) rather than to H(2) or H(3), a conclusion which ruled out structures **IIIa,b**. The calculated H(8)–H(10a) and H(2)–H(10a) distances are 2.54 and 5.37 Å, respectively, very consistent with the NOE data and the structural conclusion drawn therefrom. The conclusion, drawn from the NOE data, that Ph(2), Ph(3), and Ph(4) all lie near the Cp ring but that Ph(1) is oriented well away from Cp is also borne out by the structure shown in Figure 8.

The energy difference between the η^5 and η^3-κPPh$_2$ chelate structures is rather small, 1–3 kcal/mol, depending on the level of calculation, and our final "best estimate" for the free energy difference in solution is actually 3.2 kcal/mol in favor of the η^5 structure. The difference is well within the limits of computational uncertainty, and we can only conclude that the two structures are close in energy. The η^5 structure, with its larger flexibility of the dangling –PPh$_2$ group, is slightly favored by entropy contributions (the enthalpy difference is only 1.4 kcal/mol). For the simplified model system bearing PH$_2$ groups, we calculate a very similar energy difference ($\Delta\Delta G$ = 3.8 kcal/mol, $\Delta\Delta H$ = 2.6 kcal/mol) in favor of the η^5 structure.

Lying about 13 kcal/mol higher than the η^3-κPPh$_2$ chelate structure discussed above is an η^3 structure which, surprisingly, is neither **IIIa** nor **IIIb**. Rather, it is the complex [CpRu(2,3,4-η^3-1-$C_9H_6PPh_2CH_2$-κPPh$_2$]PF$_6$ (**IIId**), which contains a six-membered ring. In this the average of the Ru–C(2), Ru–C(3), and Ru–C(4) bonds is 2.52 Å, while the Ru–C(1) and Ru–C(9) distances are both calculated to be >3.2 Å. Attempts were made to investigate the slipped 1,2,3-η^3 isomer **IIIb**, but surprisingly, a local minimum could not be found and we suspect none exists because of steric crowding and ring strain.

CONCLUSIONS

The ylidic ligand 1-$C_9H_6PPh_2CH_2PPh_2$, readily prepared from 1-bromoindene and dppm, can potentially bind to metals in a variety of coordination modes. NMR experiments strongly suggest that the kinetic product from reaction of 1-$C_9H_6PPh_2CH_2PPh_2$ with [CpRu(MeCN)$_3$]PF$_6$ is the sandwich complex [CpRu(η^5-**I**)]PF$_6$ (**II**), containing the 1-$C_9H_6PPh_2CH_2PPh_2$ coordinated via the five-membered ring in an η^5 fashion and with a dangling –PPh$_2$ group. In solution, slow isomerization occurs to a thermodynamic product in which the phosphine moiety coordinates to the ruthenium. A combination of NMR spectroscopy and DFT calculations has allowed the elucidation of an unexpected 1,9,8-η^3 coordination mode of the 1-$C_9H_6PPh_2CH_2PPh_2$. The preference for this structure over the expected 1,2,3-η^3 coordination mode is most likely caused by constraints imposed by the ligand framework.

EXPERIMENTAL SECTION

All syntheses were carried out under dry, deoxygenated argon using standard Schlenk line techniques. Argon was deoxygenated by passage through a heated column of BASF copper catalyst and then dried by passing through a column of activated 4A molecular sieves. NMR spectra were recorded using Bruker AV500 and AV600 spectrometers, ^{1}H and ^{13}C NMR data being referenced to TMS via the residual proton signals of the deuterated solvent and ^{31}P data to external phosphoric acid. [Ru(η^5-C_5H_5)(MeCN)$_3$]PF$_6$[9] was purchased from Strem Chemicals, while 1-bromoindene was prepared via cleavage of the carbon–silicon bond of 1-trimethylsilylindene by dioxane dibromide.[12]

Synthesis of (1-$C_9H_7PPh_2MePPh_2$)Br. To a solution of 1.24 g of dppm (3.22 mmol) in 50 mL of toluene was added dropwise 0.88 g of 1-bromoindene[12] (4.52 mmol). The resulting reaction mixture was stirred at room temperature for 24 h as an off-white precipitate formed. The precipitate was filtered off, washed with toluene (3 × 5 mL) and hexanes (2 × 5 mL), and then dried in vacuo for 1 h to give 1.2 g (74% yield) of off-white product. ^{1}H NMR of isomer **A** (CD_2Cl_2, 600 MHz): δ 4.94 (t, J = 14.4 Hz, $Ph_2P^+CH_aH_bPPh_2$), 4.53 (t, J = 14.4 Hz, $Ph_2P^+CH_aH_bPPh_2$), 6.60 (m, C=CHCHP$^+$Ph$_2$), 6.86 (m, CH=CHCHP$^+$Ph$_2$), 7.23 (overlap, C=CHCHP$^+$PH$_2$), 7.05–8.11 (m, aromatic). ^{31}P NMR of isomer **A** (CD_2Cl_2): δ 30.4 (d,

$P^+Ph_2CH_2PPh_2$), −25.6 (d, $P^+Ph_2CH_2PPh_2$). ^1H NMR of isomer **B** (CD_2Cl_2, 600 MHz): δ 4.48 (d, J = 14.3 Hz, $CHP^+Ph_2CH_2PPh_2$), 3.80 (s, $CH_2CH{=}CP^+Ph_2CH_2PPh_2$) 8.05 (d, $CH_2CH{=}CP^+PH_2$), 7.05–8.11(m, aromatic). ^{31}P NMR of isomer **B** (CD_2Cl_2): δ 14.4 (d, $P^+PH_2CH_2PPh_2$), −25.5 (d, $P^+Ph_2CH_2PPh_2$).

Synthesis of 1-$C_9H_6PPh_2MePPh_2$ (I). A mixture of 2.23 g of (1-$C_9H_7PPh_2MePPh_2$)Br (4.46 mmol) and 0.12 g of NaH (5 mmol) in 40 mL of THF was stirred for 12 h, turning green and then brown. The resulting mixture was filtered through Celite, and the solvent was removed under reduced pressure to give a brown solid which was redissolved in a minimum amount of CH_2Cl_2 and reprecipitated by layering with hexanes (hexanes/CH_2Cl_2 4/1). The resulting precipitate was filtered, washed with methanol, and dried to give 1.76 g (79% yield) of green, air-sensitive **II**. X-ray-quality crystals were obtained by layering a saturated solution of **II** in CH_2Cl_2 with hexanes. ^1H and ^{13}C NMR data are given in Table 1. ^{31}P NMR (CD_2Cl_2): δ 7.52 (d, J_{PP} = 61 Hz, $P^+PH_2CH_2PPh_2$), −28.3 (d, $P^+Ph_2CH_2PPh_2$).

Synthesis of Isomers of [CpRu(1-$C_9H_7PPh_2MePPh_2$)]PF_6. A solution containing 0.01 g of [CpRu(MeCN)$_3$]PF_6 and 0.012 g of **I** in 0.6 mL of CD_2Cl_2 quickly turned red. Monitoring the ^1H and ^{31}P NMR spectra over several days revealed two products, the apparent kinetic product **II** and the thermodynamic product **III**. Initially the ratio of **II** to **III** was very nearly 1:1 but, after 10 days, **II** was no longer present and the amount of **III** had increased relative to the solvent peak. ^1H and ^{13}C NMR data can be found in Table 1.

Computational Methods. Geometries of complexes **II** and **III** and of simplified versions bearing H instead of Ph substituents at P were optimized at the b3-lyp[13]/TZVP[14] level using the Turbomole program[15] coupled to an external optimizer.[16] For the chelate isomer, several discrete local minima were located, differing in the indenyl carbons bound to the Ru atom; only the lowest energy structure is discussed in the text. Final geometries were checked by a vibrational analysis (no imaginary frequencies), which was also used to calculate thermal corrections (enthalpy and entropy). Single-point calculations were then carried out with a larger basis set (TZVPP[17]) and inclusion of an electronic correction for solvent effects using COSMO[18] (ε = 9.1, CH_2Cl_2). These improved energies were combined with the above thermal corrections (entropy scaled by 0.67 to account for reduced freedom of motion in solution[19]) to obtain the final free energies mentioned in the text.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables, figures, and CIF files giving crystallographic details for 1-$C_9H_6PPh_2CH_2PPh_2$ (**I**) and (1-C_9H_7dppm)Br, including figures showing complete numbering schemes, thermal ellipsoid figures, and tables of positional and thermal parameters, bond lengths, and bond angles, and energy calculations for compounds **II** and **IIIc,d** (Table S1) and of the *xyz* coordinates used in the theoretical calculations (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic data for 1-$C_9H_6PPh_2CH_2PPh_2$ (CCDC 892305) and (1-C_9H_7dppm)Br (CCDC 892303) may also be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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