5626 *Inorg. Chem.* **2001,** *40,* 5626−5635

Synthesis and Structural Characterization of PhP[(C_5Me_4)$_2$], a Monodentate Chiral Phosphine Derived from Intramolecular C−C Coupling of Tetramethylcyclopentadienyl Groups: An Evaluation of Steric and Electronic Properties

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The chiral monodentate phosphine PhP[(C_5Me_4)$_2$] is readily obtained by oxidation of the lithium complex Li_2[PhP(C_5Me_4)$_2$] with I_2, which couples the two cyclopentadienyl groups to form a five-membered heterocyclic ring. The steric and electronic properties of PhP[(C_5Me_4)$_2$] have been evaluated by X-ray diffraction and IR spectroscopic studies on a variety of derivatives, including Ph[(C_5Me_4)$_2$]PE (E = S, Se), Cp*MCl_4{P[(C_5Me_4)$_2$]-Ph} (M = Mo, Ta), Ir{P[(C_5Me_4)$_2$]Ph}$_2$(CO)Cl, and CpFe(CO){PhP[(C_5Me_4)$_2$]}Me. For comparison purposes, derivatives of the related phospholane ligand PhP[$Me_2C_4H_6$] have also been investigated, including Ph[$Me_2C_4H_6$]-PS, Ir{Ph[$Me_2C_4H_6$]}$_2$(CO)Cl, Ir{Ph[$Me_2C_4H_6$]}$_2$(CO)Me, Ir{PPh[$Me_2C_4H_6$]}(COD)(Cl), and Pd{P[$Me_2C_4H_6$]-Ph}[η^2-C_6H_4C(H)(Me)NMe_2]Cl. The steric and electronic properties of PhP[(C_5Me_4)$_2$] are determined to be intermediate between those of PPh_2Me and PPh_3. Thus, the crystallographic cone angles increase in the sequence PPh_2Me (134.5°) < PhP[(C_5Me_4)$_2$] (140.2°) < PPh_3 (148.2°), while the electron donating abilities decrease in the sequence PPh_2Me > PhP[(C_5Me_4)$_2$] > PPh_3. Finally, PhP[(C_5Me_4)$_2$] has a smaller cone angle and is less electron donating than the structurally similar phosphine, PhP[$Me_2C_4H_6$].

Introduction

Tertiary phosphine ligands are a prominent feature of inorganic chemistry.[1] Their ubiquity is a consequence of the fact that the phosphorus substituents have a significant impact on the steric and electronic properties of the phosphine ligand, which thereby influences the chemistry of the metal center to which it is attached. Furthermore, the use of enantiomerically pure chiral phosphines has had a profound influence on the field of asymmetric catalysis,[2] as illustrated by the commercial synthesis of L-DOPA.[3] In this paper, we report the synthesis and structural characterization of a new chiral phosphine, PhP[(C_5Me_4)$_2$] (Figure 1), and present an evaluation of its steric and electronic properties.

Results and Discussion

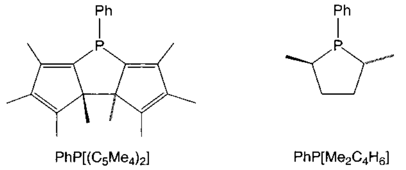

Figure 1. PhP[(C_5Me_4)$_2$] and PhP[$Me_2C_4H_6$] ligands.

Much attention has been directed towards the synthesis and application of new multidentate phosphine ligands, particularly with respect to their use in asymmetric catalysis.[2,4] Multidentate phosphine ligands have received more attention than their monodentate counterparts because it is generally considered that the former frequently exhibit greater degrees of asymmetric induction.[5] This observation is often rationalized by the notion that chelation inhibits rotation about the metal-phosphorus bond and thereby provides greater stereocontrol. Recently, however, useful applications of chiral monophosphines and related ligands in asymmetric organometallic catalysis have been recognized.[6] For example, monodentate biarylphosphonite ligands derived from 2,2′-binaphthol and 9,9′-biphenanthrol have been demonstrated to be superior to bidentate counterparts in certain instances.[7,8] Furthermore, monodentate phosphine ligands continue to be employed as important catalyst components for a variety of organic transformations,[9] and so it is evident that the synthesis of new phosphine ligands with unusual structures is

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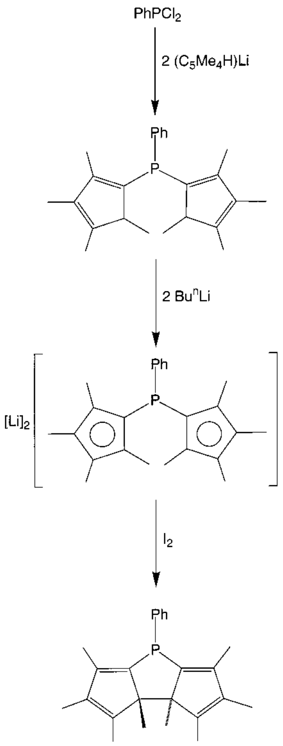
Scheme 1



of relevance to both catalysis and coordination chemistry. For this reason, we report here the synthesis and structural characterization of the chiral phosphine PhP[$(C_5Me_4)_2$].

The phosphine PhP[$(C_5Me_4)_2$] is readily obtained by oxidation of the lithium complex Li_2[PhP$(C_5Me_4)_2$][10] with I_2, which couples the cyclopentadienyl groups to form a five-membered heterocyclic ring (Scheme 1). While phospholane derivatives are common, they are not generally prepared by a C−C coupling reaction.[11] The C−C coupling reaction also occurs in an asymmetric manner, such that the two methyl groups of the ring junction adopt a trans, rather than cis, disposition. The asymmetric nature of the coupling is readily indicated by the observation that PhP[$(C_5Me_4)_2$] is characterized by distinct signals for the eight inequivalent methyl groups in the ^{1}H NMR spectrum, only two of which overlap. The molecular structure of PhP[$(C_5Me_4)_2$] has been determined by X-ray diffraction, as illustrated in Figure 2, thereby confirming the chiral nature of the compound.[12,13,14]

The influence of a tertiary phosphine on a metal center is dictated by its steric and electronic properties. The size of a phosphine ligand has traditionally been classified by its cone angle, as originally described by Tolman.[15] While the Tolman cone angles were calculated using idealized space-filling CPK models, Mingos has recently reported a simple algorithm that allows calculation of cone angles from crystallographic data, so-called “crystallographic cone angles”. [16,17] Therefore, to assess the steric properties of PhP[$(C_5Me_4)_2$], we have synthesized several derivatives, namely Ph[$(C_5Me_4)_2$]PE (E = S, Se), Cp*MCl_4{P[$(C_5Me_4)_2$]Ph} (M = Mo, Ta),[18] and Ir{P[$(C_5Me_4)_2$]-Ph}$_2$(CO)Cl (Schemes 2 − 4), and determined their structures by X-ray diffraction (Figures 3 − 7). The most extensive comparison can be made for the sulfido and selenido complexes Ph[$(C_5Me_4)_2$]PE (E = S, Se), since a large variety of R_3PE derivatives have been structurally characterized. As would be expected, the P═S bond length in Ph[$(C_5Me_4)_2$]PS [1.965(1) Å] is comparable to the mean value of 1.95 Å for structurally characterized analogues listed in the Cambridge Structural Database (CSD);[19] likewise, the P═Se bond length in Ph-[$(C_5Me_4)_2$]PSe [2.126(1) Å] compares favorably with the CSD mean value of 2.10 Å.

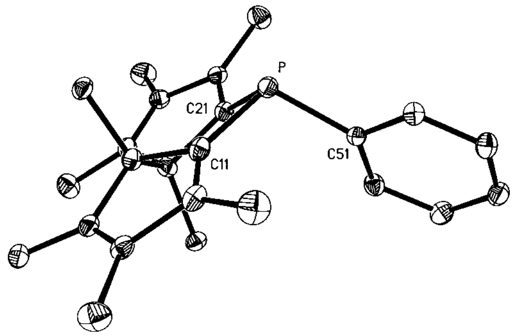


Figure 2. Molecular structure of PhP[$(C_5Me_4)_2$]. Selected bond lengths (Å) and angles (deg): P−C(11) 1.828(3), P−C(21) 1.815(3), P−C(51) 1.827(3), C(15)−C(25) 1.559(4); C(11)−P−C(21) 87.8(1), C(11)−P−C(51) 106.2(1), C(21)−P−C(51) 106.5(1).

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(12) The enantiomers of PhP[$(C_5Me_4)_2$] may be separated using a Chiralpak AD analytical column eluted with 0.7% 2-propanol in hexane at a rate of 0.5 mL per min. We thank Professor S. L. Buchwald and Dr. J. M. Fox for determining these conditions.

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(18) Complexes of the type $(Cp^R)MCl_4(PR_3)$ are known for a variety of metals, including Nb,[a] Ta,[b] Mo,[c−g] W,[c] and Re.[h] See: (a) Fettinger, J. C.; Keogh, D. W.; Poli, R. *Inorg. Chem.* **1995**, *34*, 2343−2347. (b) Hadi, G. A. A.; Fromm, K.; Blaurock, S.; Jelonek, S.; Hey-Hawkins, E. *Polyhedron* **1997**, *16*, 721−731. (c) Murray, R. C.; Blum, L.; Liu, A. H.; Schrock, R. R. *Organometallics* **1985**, *4*, 953−954. (d) Felsberg, R.; Blaurock, S.; Jelonek, S.; Gelbrich, T.; Kirmse, R.; Voigt, A.; Hey-Hawkins, E. *Chem. Ber.-Recl.* **1997**, *130*, 807−812. (e) Morise, X.; Green, M. L. H.; McGowan, P. C.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1994**, 871−878. (f) MacLaughlin, S. A.; Murray, R. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1985**, *4*, 796−798. (g) Harlan, C. J.; Jones, R. A.; Koschmieder, S. U.; Nunn, C. M. *Polyhedron* **1990**, *9*, 669−679. (h) Herrmann, W. A.; Voss, E.; Küsthardt, U.; Herdtweck, E. *J. Organomet. Chem.* **1985**, *294*, C37−C40.

Table 1. Crystallographic Cone Angles for $PhP[(C_5Me_4)_2]$ and $PhP[Me_2C_4H_6]$ in Their Complexes

compound	cone angle (deg)	average cone angle (deg)
$Ph[(C_5Me_4)_2]PS$	172.4	171.8
$Ph[(C_5Me_4)_2]PSe$	171.1	
$Cp^*MoCl_4\{P[(C_5Me_4)_2]Ph\}$	138.8	140.2
$Cp^*TaCl_4\{P[(C_5Me_4)_2]Ph\}$	140.3	
$Ir\{P[(C_5Me_4)_2]Ph\}_2(CO)Cl$	141.4[a]	
$Ph[Me_2C_4H_6]PO$	153.8	149.7
$Ph[Me_2C_4H_6]PS$	149.7	
$Ir\{P[Me_2C_4H_6]Ph)_2(CO)Me$	148.3[b]	
$Ir\{P[Me_2C_4H_6]Ph)_2(CO)Cl$	147.5[b]	
$Ir\{P[Me_2C_4H_6]Ph)(COD)Cl$	150.1	
$Pd\{P[Me_2C_4H_6]Ph)[\eta^2-C_6H_{4C}(H)(Me)NMe_2]$	148.6	

[a] Since one of the phosphine ligands is disordered, the value listed is that for the ordered one. [b] Average values.

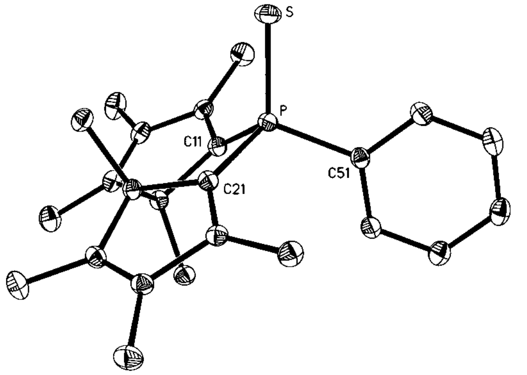

Figure 3. Molecular structure of $Ph[(C_5Me_4)_2]PS$. Selected bond lengths (Å) and angles (deg): P−S 1.965(1), P−C(11) 1.800(2), P−C(21) 1.785(2), P−C(51) 1.814(2); S−P−C(11) 115.4(1), S−P−C(21) 116.3(1), S−P−C(51) 111.5(1).

The determination of the crystallographic cone angle of $PhP[(C_5Me_4)_2]$ in one of its derivatives requires the ligated atom to be artificially shifted along the M−P bond vector to a position 2.28 Å from the phosphorus atom.[16] This procedure allows comparison with the original Tolman values that were derived using a model in which the phosphine was attached to a nickel center with a Ni−P bond length of 2.28 Å. The data presented in Table 1 indicate that the crystallographic cone angle of $PhP[(C_5Me_4)_2]$ in these complexes varies over quite a large range, from 138.8° to 172.4°. However, it is clear that the complexes fall into two categories, namely the chalcogenido complexes, $Ph[(C_5Me_4)_2]PE$ (E = S, Se), and the metal complexes, $Cp^*MCl_4\{P[(C_5Me_4)_2]Ph\}$ (M = Mo, Ta), and $Ir\{P[(C_5Me_4)_2]Ph\}_2(CO)Cl$. The chalcogenido complexes have the greater values because the absence of substituents on the chalcogen means that the phenyl group can rotate to a position that minimizes intraligand repulsions.[20] The metal complexes, in contrast, have smaller cone angles because the phenyl group rotates about the P−Ph bond to a position that minimizes interactions with the ligands attached to the metal. For comparison, the conformations of $PhP[(C_5Me_4)_2]$ in its various derivatives are illustrated in Figure 8.

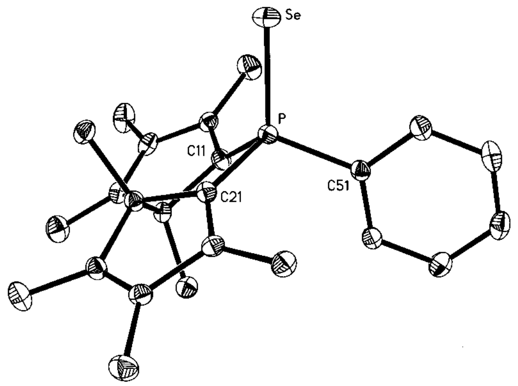

Figure 4. Molecular structure of $Ph[(C_5Me_4)_2]PSe$. Selected bond lengths (Å) and angles (deg): P−Se 2.126(1), P−C(11) 1.813(3), P−C(21) 1.783(3), P−C(51) 1.823(3); Se−P−C(11) 115.6(1), Se−P−C(21) 115.9(1), Se−P−C(51) 111.9(1).

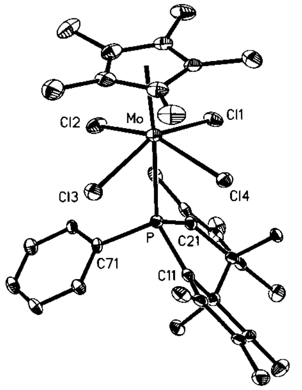

Figure 5. Molecular structure of $Cp^*MoCl_4\{P[(C_5Me_4)_2]Ph\}$. Selected bond lengths (Å): Mo−Cl(1) 2.296(3), Mo−Cl(2) 2.300(3), Mo−Cl(3) 2.294(3), Mo−Cl(4) 2.321(3), Mo−P 2.627(3).

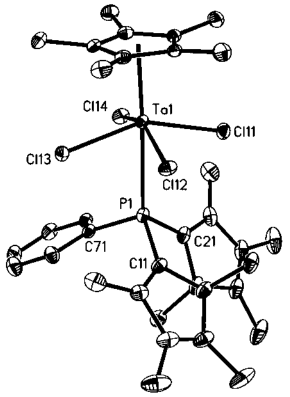

Figure 6. Molecular structure of $Cp^*TaCl_4\{P[(C_5Me_4)_2]Ph\}$ (only one of the crystallographically independent molecules is shown). Selected bond lengths (Å): Ta(1)−Cl(11) 2.391(1), Ta(1)−Cl(12) 2.391(1), Ta(1)−Cl(13) 2.403(1), Ta−Cl(14) 2.387(1), Ta(1)−P(1) 2.832(1), Ta(2)−Cl(21) 2.411(1), Ta(2)−Cl(22) 2.401(1), Ta(2)−Cl(23) 2.380(1), Ta(2)−Cl(24) 2.382(1), Ta(2)−P(2) 2.803(1).

The crystallographic cone angle of $PhP[(C_5Me_4)_2]$ in its metal complexes varies over the narrow range 138.8° to 141.4°, averaging 140.2°. It is, therefore, evident that it is the latter value that is best representative of the cone angle for $PhP[(C_5Me_4)_2]$ as applied to transition metal chemistry. For comparison, cone angle data for other phosphines are listed in Table 2, thereby demonstrating that the value for $PhP[(C_5Me_4)_2]$ is intermediate between that of PPh_2Me (134.5°) and PPh_3 (148.2°). It is also pertinent to compare the steric properties of

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(19) CSD Version 5.20. *3D Search and Research Using the Cambridge Structural Database*, Allen, F. H.; Kennard, O. *Chem. Design Automation News* **1993**, *8 (1)*, 1, 31−37.

(20) Furthermore, the crystallographic cone angle calculated for the uncomplexed $PhP[(C_5Me_4)_2]$ ligand is 163.9°. This value was determined by placing a hypothetical atom 2.28 Å from the phosphorus atom in the remaining tetrahedral position as determined by SHELXTL.

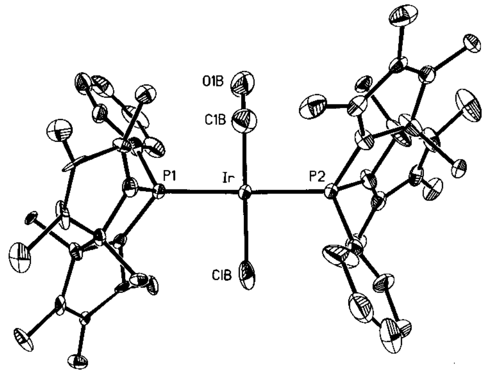

Figure 7. Molecular structure of Ir{P[(C_5Me_4)$_2$]Ph}$_2$(CO)Cl. The CO and Cl ligands are disordered, as is the phosphine configuration at P(1). Selected bond lengths (Å): Ir−P(1) 2.315(2), Ir−P(2) 2.314(2), Ir−Cl$_{av}$ 2.31, Ir−C$_{av}$ 1.94 (see text).

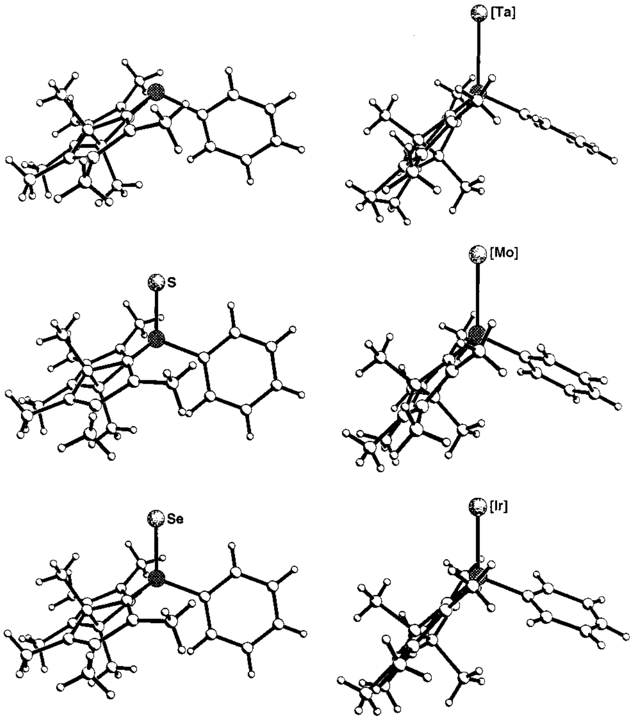

Figure 8. Conformations of the PhP[(C_5Me_4)$_2$] ligand in PhP[(C_5Me_4)$_2$], Ph[(C_5Me_4)$_2$]PS, Ph[(C_5Me_4)$_2$]PSe, Cp*TaCl$_4${P[(C_5Me_4)$_2$]Ph}, Cp*MoCl$_4${P[(C_5Me_4)$_2$]Ph}, and Ir{P[(C_5Me_4)$_2$]Ph}$_2$(CO)Cl.

Table 2. Comparison of Cone Angles for Selected Phosphines in Transition Metal Complexes[a]

	crystallographic cone angle (deg)	Tolman cone angle (deg)
PMe_3	111.1	118
PEt_3	137.3	132
PCy_3	160.1	170
$PPhMe_2$	119.9	122
PPh_2Me	134.5	136
PPh_3	148.2	145
PhP[(C_5Me_4)$_2$]	140.2	
PhP[$Me_2C_4H_6$]	149.7	

[a] With the exception of PhP[(C_5Me_4)$_2$] and PhP[$Me_2C_4H_6$], all data taken from refs 15 and 16.

PhP[(C_5Me_4)$_2$] with that of PhP[$Me_2C_4H_6$],[21,22] a structurally similar phosphine (Figure 1).

Interestingly, although PhP[$Me_2C_4H_6$] is readily available in enantiomerically pure form, PhP[(2*R*,5*R*)−$Me_2C_4H_6$],[21] its applications have been almost completely unexplored, and there

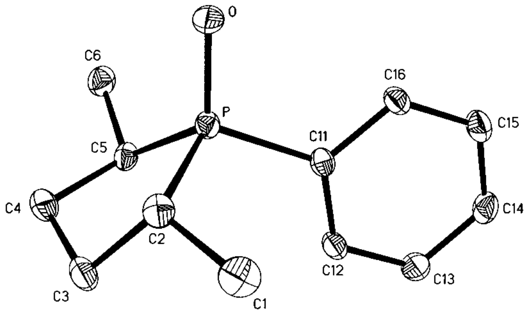

Figure 9. Molecular structure of Ph[*R*,*R*-$Me_2C_4H_6$]PO. Selected bond lengths (Å) and angles (deg): P−O 1.489(3), P−C(2) 1.821(4), P−C(5) 1.828(4), P−C(11) 1.822(3); O−P−C(2) 114.7(2), O−P−C(5) 115.8(2), O−P−C(11) 111.0(2).

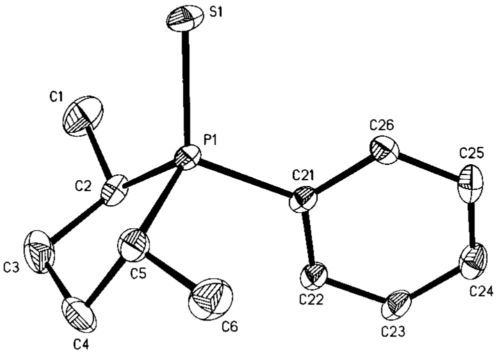

Figure 10. Molecular structure of Ph[*R*,*R*-$Me_2C_4H_6$]PS (only one of the crystallographically independent molecules is shown). Selected bond lengths (Å) and angles (deg): P(1)−S(1) 1.952(2), P(1)−C(2) 1.828(5), P(1)−C(5) 1.832(5), P(1)−C(21) 1.817(5), P(2)−S(2) 1.953(2), P(2)−C(12) 1.833(5), P(2)−C(15) 1.849(5), P(2)−C(31) 1.813(5); S(1)−P(1)-C(2) 116.7(2), S(1)−P(1)-C(5) 114.8(2), S(1)−P(1)-C(21) 113.3(2), S(2)−P(2)-C(12) 113.8(2), S(2)−P(2)-C(15) 115.7(2), S(2)−P(2)-C(31) 112.7(2).

are no structurally characterized derivatives listed in the Cambridge Structural Database. Determination of the cone angle of PhP[$Me_2C_4H_6$], therefore, required the synthesis of several derivatives, as illustrated in Schemes 2 − 5. Of these complexes, the structures of Ph[*R*,*R*-$Me_2C_4H_6$]PO (Figure 9),[23] Ph[*R*,*R*-$Me_2C_4H_6$]PS (Figure 10), Ir{Ph[*R*,*R*-$Me_2C_4H_6$]}$_2$(CO)Cl (Figure 11), Ir{Ph[*R*,*R*-$Me_2C_4H_6$]}$_2$(CO)Me (Figure 12), Ir{PPh[*R*,*R*-$Me_2C_4H_6$]}(COD)(Cl) (Figure 13), and Pd{P[*R*,*R*-$Me_2C_4H_6$]Ph}[η^2-C_6H_4C(H)(Me)NMe_2]Cl (Figure 14) were determined by X-ray diffraction. Examination of these structures indicates that the crystallographic cone angle for the PhP[$Me_2C_4H_6$] ligand shows little variation (147.5−150.1°), and has an average value of 149.7° (Table 1). As such, PhP[(C_5Me_4)$_2$] is less sterically demanding than PhP[$Me_2C_4H_6$].

It is also appropriate to emphasize that the structures of Ph[*R*,*R*-$Me_2C_4H_6$]PS, Ir{Ph[*R*,*R*-$Me_2C_4H_6$]}$_2$(CO)Cl, Ir{Ph[*R*,*R*-$Me_2C_4H_6$]}$_2$(CO)Me, Ir{PPh[*R*,*R*-$Me_2C_4H_6$]}(COD)(Cl), and Pd{P[*R*,*R*-$Me_2C_4H_6$]Ph}[*S*-η^2-C_6H_4C(H)(Me)NMe_2]Cl were determined using enantiomerically pure phosphine, PhP[*R*,*R*-

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(21) (a) Wilson, S. R.; Pasternak, A. *Synlett.* **1990**, 199−200. (b) Burk, M. J.; Feaster, J. E.; Harlow, R. L. *Organometallics* **1990**, *9*, 2653−2655. (c) Burk, M. J.; Feaster, J. E.; Harlow, R. L. *Tetrahedron: Asymmetry* **1991**, *2*, 569−592. (d) Nandi, M.; Jin, J.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1999**, *121*, 9899−9900.

(22) For related bis and tris phospholane derivatives, see ref 2 and: (a) Burk, M. J.; Harlow, R. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1462−1464. (b) Burk, M. J.; Feaster, J. E.; Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1993**, *115*, 10125−10138.

(23) The structure of Ph[$Me_2C_4H_6$]PO has been cited, but no details were reported. See ref 21a.

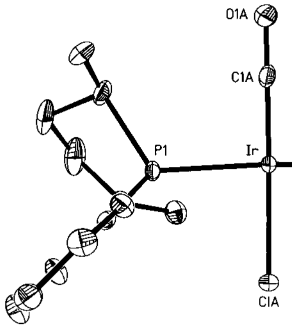


Figure 11. Molecular structure of Ir{Ph[*R*,*R*-$Me_2C_4H_6$]}$_2$(CO)Cl. The CO and Cl ligands are disordered. Selected bond lengths (Å): Ir−P(1) 2.315(2), Ir−P(2) 2.334(2), Ir−C(1_{av}) 1.75, Ir−Cl_{av} 2.37 Å (see text).

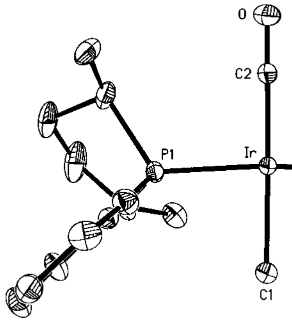


Figure 12. Molecular structure of Ir{Ph[*R*,*R*-$Me_2C_4H_6$]}$_2$(CO)Me. Selected bond lengths (Å) and angles (deg): Ir−C(1) 2.134(4), Ir−C(2) 1.832(4), Ir−P(1) 2.272(1), Ir−P(2) 2.293(1), C(2)−O 1.150(5); C(1)−Ir−P(1) 86.6(1), P(1)−Ir−C(2) 92.7(1), C(2)−Ir−P(2) 92.7(1).

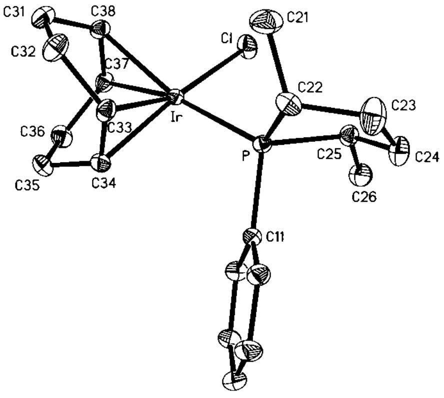


Figure 13. Molecular structure of Ir{PPh[*R*,*R*-$Me_2C_4H_6$]}$_2$(COD)(Cl). Selected bond lengths (Å): Ir−Cl 2.347(1), Ir−P 2.311(1), Ir−C(33) 2.106(4), Ir−C(34) 2.111(4), Ir−C(37) 2.207(4), Ir−C(38) 2.196(4).

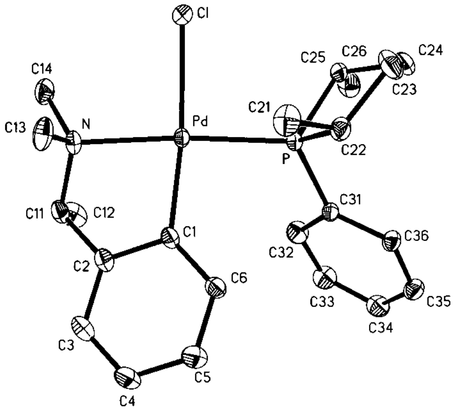
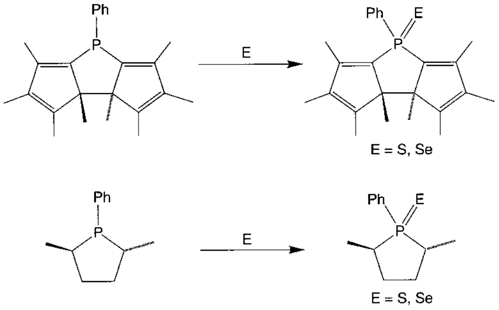
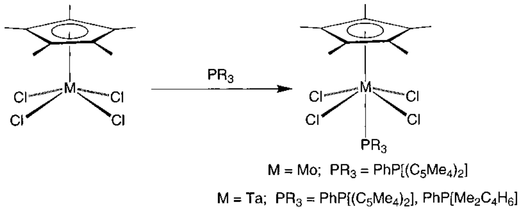


Figure 14. Molecular structure of Pd{P[*R*,*R*-$Me_2C_4H_6$]Ph}[*S*-η^2-$C_6H_4C(H)(Me)NMe_2$]Cl. Selected bond lengths (Å) and angles (deg): Pd−C(31) 2.017(2), Pd−N 2.158(2), Pd−Cl 2.424(1), Pd−P 2.253(1); C(31)−Pd−N 81.40(7), N−Pd−Cl 92.86(5), Cl−Pd−P 91.67(2), P−Pd−C(31) 94.18(5).

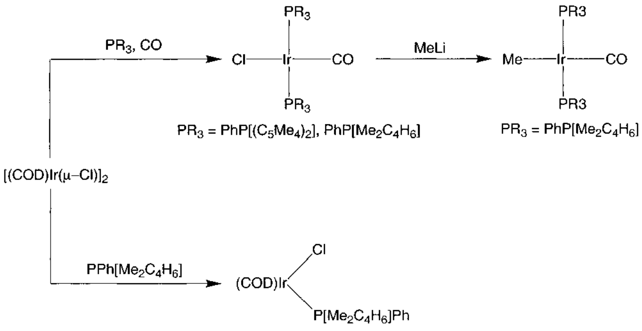
Scheme 2



Scheme 3



Scheme 4



$Me_2C_4H_6$]. The high quality of the structure determinations, together with the known *S*-configuration of the carbon atom (C*) of the [η^2-*C*,*N*-$C_6H_4C^*(H)(Me)NMe_2$] ligand,[24] provides definitive proof for the *R*,*R*-configurations of the two α-ring carbon atoms in the chiral phosphine PhP[*R*,*R*-$Me_2C_4H_6$]. Prior to this result, the *R*,*R*-configuration was inferred by assuming the configurational transformations proposed in Scheme 6. In this regard, we have also structurally characterized the optically active sulfate precursor, [(2*S*,5*S*)−$Me_2C_4H_6(O_2SO_2)$], and have thereby confirmed the proposed configuration.

The electronic properties of phosphine ligands are as diverse as their steric properties and are frequently classified by determining the impact on the ν(CO) stretching frequency of a metal carbonyl complex.[15,25,26] Consideration of ν(CO) for a series of *trans*-Ir(PR_3)$_2$(CO)Cl complexes places the electron donating ability of PhP[(C_5Me_4)$_2$] as intermediate between PPh_2Me and PPh_3. Thus, the electron donating abilities of these phosphines, as judged by the ν(CO) stretching frequen-

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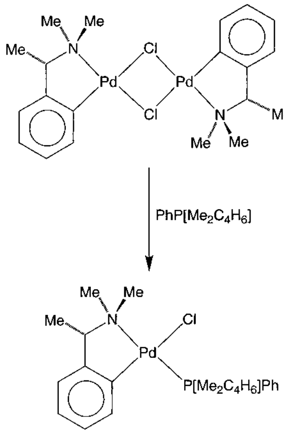
(24) For studies pertaining to the configuration of the precursor, {Pd-[*S*-η^2-*C*,*N*-$C_6H_4C^*(H)(Me)NMe_2$](μ-Cl)}$_2$, derived from the reaction of $[PdCl_4]^{2-}$ with (*S*)-PhCH(Me)NMe_2, see: (a) Tani, K.; Brown, L. D.; Ahmed, J.; Ibers, J. A.; Yokata, M.; Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1977**, *99*, 7876−7886. (b) Otsuka, S.; Nakamura, A.; Kano, T.; Tani, K. *J. Am. Chem. Soc.* **1971**, *93*, 4301−4303.

(25) Verkade, J. G. *Coord. Chem. Rev.* **1972/73**, *9*, 1−106.

Scheme 5



Scheme 6

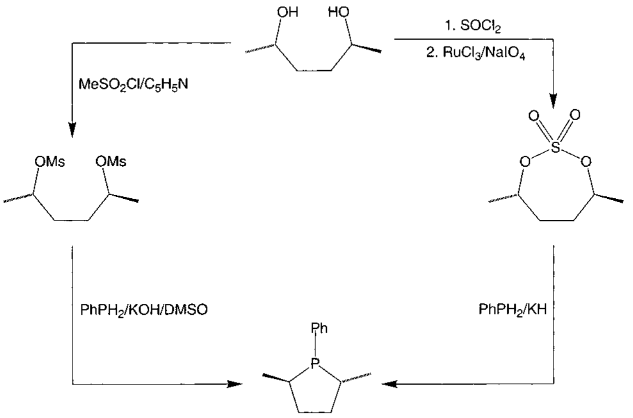


Table 3. Comparison of ν(CO) for Selected *trans*-Ir(PR$_3$)$_2$(CO)Cl Complexes

PR$_3$	ν(CO)/cm^{-1} (Nujol)
PMe$_3$	1938,[a] 1943[b]
PEt$_3$	1929,[a] 1944[b]
PPhMe$_2$	1960,[a] 1954,[b] 1957[c]
PPh$_2$Me	1950[b]
PPh$_3$	1961[d]
PhP[(C$_5$Me$_4$)$_2$]	1955
PhP[Me$_2$C$_4$H$_6$]	1937

[a] Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. (A)* **1968**, 1887−1889. [b] Field, L. D.; Lawrenz, E. T.; Ward, A. J. *Polyhedron* **1999**, *18*, 3031−3034. [c] Smith, L. R.; Lin, S. M.; Chen, M. G.; Mondal, J. U.; Blake, D. M. *Inorg. Synth.* **1982**, *21*, 97−99. [d] Collman, J. P.; Sears, C. T., Jr.; Kubota, M. *Inorg. Synth.* **1990**, *28*, 92−94.

cies of Ir(PR$_3$)$_2$(CO)Cl in Nujol (Table 3), decrease in the following sequence: PPh$_2$Me (1950 cm^{-1}) > PhP[(C$_5$Me$_4$)$_2$] (1955 cm^{-1}) > PPh$_3$ (1961 cm^{-1}). A similar consideration for Ir{PPh[Me$_2$C$_4$H$_6$]}$_2$(CO)Cl indicates that PhP[(C$_5$Me$_4$)$_2$] is less electron donating than PhP[Me$_2$C$_4$H$_6$]. ν(CO) stretching frequencies for a series of CpFe(PR$_3$)(CO)Me derivatives have also been used as an indicator of electron donating ability.[26] In this regard, ν(CO) for CpFe{P[Me$_2$C$_4$H$_6$]Ph}(CO)Me (1914 cm^{-1}) and CpFe{P[(C$_5$Me$_4$)$_2$]Ph}(CO)Me (1921 cm^{-1}) also indicate that PhP[(C$_5$Me$_4$)$_2$] is less electron donating than PhP[Me$_2$C$_4$H$_6$].

The aforementioned coordination of PhP[(C$_5$Me$_4$)$_2$] and PhP[Me$_2$C$_4$H$_6$] to Cp*TaCl$_4$ is reversible, and treatment of Cp*TaCl$_4${P[(C$_5$Me$_4$)$_2$]Ph} and Cp*TaCl$_4${P[Me$_2$C$_4$H$_6$]Ph} with PR$_3$ generates Cp*TaCl$_4$(PR$_3$) (PR$_3$ = PPh$_2$Me, PPhMe$_2$). A consideration of the equilibria for the various exchange reactions indicates that the strength of the Ta−PR$_3$ interaction increases in the sequence PPh$_3$[27] $\ll$ PhP[(C$_5$Me$_4$)$_2$] < PhP[Me$_2$C$_4$H$_6$] < PPh$_2$Me $\ll$ PPhMe$_2$. Since PhP[Me$_2$C$_4$H$_6$] has a larger cone angle than PhP[(C$_5$Me$_4$)$_2$], it is evident that the stronger binding of the former ligand is a consequence of its greater electron donating ability.

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum or Schlenk techniques.[28] Solvents were purified and degassed by standard procedures. NMR spectra were recorded on Bruker Avance 300wb DRX, Bruker Avance 400 DRX, and Bruker Avance 500 DMX spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to SiMe$_4$ (δ = 0) and were referenced internally with respect to the protio solvent impurity or the ^{13}C resonances, respectively. ^{31}P NMR spectra are referenced relative to 85% H$_3$PO$_4$ (δ = 0) using P(OMe)$_3$ as an external reference (δ = 141.0). All coupling constants are reported in Hz. IR spectra were recorded as KBr pellets on Perkin-Elmer 1430 or 1600 spectrophotometers and are reported in cm^{-1}. C, H, and N elemental analyses were measured using a Perkin-Elmer 2400 CHN Elemental Analyzer. {Pd[*S*-η^2-*C*,*N*-C$_6$H$_4$C*(H)(Me)NMe$_2$](μ-Cl)}$_2$ was obtained from Aldrich.

PhP[*R*,*R*-Me$_2$C$_4$H$_6$] was obtained from (2*S*,5*S*)-hexanediol (Aldrich) by the literature method,[21d] with the exception of using Bu^{n}Li instead of KH.

Synthesis of PhP[(C$_5$Me$_4$)$_2$]. A solution of I$_2$ (4.49 g, 17.69 mmol) in toluene (100 mL) was slowly added to a suspension of Li$_2$[PhP(C$_5$Me$_4$)$_2$] (8.00 g, 22.08 mmol) in toluene (150 mL) at −78 °C. The mixture was warmed to room temperature, then heated at 80 °C for 4 days. After this period, the mixture was filtered and the residue was extracted into toluene (100 mL) and filtered. The volatile components were removed from the combined filtrate in vacuo, and the resulting oily residue was extracted into pentane (200 mL) and filtered. The filtrate was concentrated (to 5 mL), cooled to −78 °C, filtered and the precipitate was dried in vacuo to give PhP[(C$_5$Me$_4$)$_2$] as a pale brown solid (3.10 g, 50% based on I$_2$). Anal. calcd for C$_{24}$H$_{29}$P: C, 82.7%; H, 8.4%. Found: C, 82.8%; H, 8.1%. IR Data (KBr disk, cm^{-1}): 3070 (m), 3055 (m), 3028 (m), 3010 (m), 2953 (vs), 2918 (vs), 2857 (vs), 2728 (m), 1638 (m), 1601 (w), 1585 (m), 1566 (s), 1480 (m), 1436 (vs), 1384 (s), 1371 (vs), 1360 (vs), 1325 (m), 1314 (m), 1275 (w), 1195 (m), 1178 (m), 1123 (w), 1111 (m), 1092 (s), 1071 (s), 1028 (m), 1013 (m), 1001 (m), 986 (m), 964 (w), 946 (w), 914 (w), 853 (w), 765 (w), 748 (vs), 701 (vs), 658 (m), 645 (m), 633 (m), 610 (m), 598 (s), 568 (m), 524 (w), 501 (s), 482 (m), 451 (s). ^{1}H NMR (C$_6$D$_6$): 0.84 [s, 3 H of C$_{10}$(C*H*$_3$)$_8$P], 0.91 [s, 3 H of C$_{10}$(C*H*$_3$)$_8$P], 1.65 [s, 3 H of C$_{10}$(C*H*$_3$)$_8$P], 1.68 [s, 3 H of C$_{10}$(C*H*$_3$)$_8$P], 1.77 [d, $^4J_{\rm P-H}$ = 4, 3 H of C$_{10}$(C*H*$_3$)$_8$P], 1.85 [s, 6 H of C$_{10}$(C*H*$_3$)$_8$P], 2.02 [d, $^4J_{\rm P-H}$ = 2, 3 H of C$_{10}$(C*H*$_3$)$_8$P], 7.07 [t, $^3J_{\rm H-H}$ = 7, 1 H of C$_6$*H*$_5$], 7.16 [t, $^3J_{\rm H-H}$ = 7, 2 H of C$_6$*H*$_5$], 7.82 [t, $^3J_{\rm P-H}$ = $^3J_{\rm H-H}$ = 8, 2 H of C$_6$*H*$_5$]. ^{13}C NMR (C$_6$D$_6$): 11.3 [q, $^1J_{\rm C-H}$ = 126, 2 C of C$_{10}$(*C*H$_3$)$_8$P], 13.3 [q, $^1J_{\rm C-H}$ = 126, 2 C of C$_{10}$(*C*H$_3$)$_8$P], 14.3 [q, $^1J_{\rm C-H}$ = 126, 1 C of C$_{10}$(*C*H$_3$)$_8$P], 14.6 [dq, $^1J_{\rm C-H}$ = 126, $^3J_{\rm P-C}$ = 10, 1 C of C$_{10}$(*C*H$_3$)$_8$P], 18.7 [q, $^1J_{\rm C-H}$ = 128, 1 C of C$_{10}$(*C*H$_3$)$_8$P], 19.1 [dq, $^1J_{\rm C-H}$ = 128, $^4J_{\rm P-C}$ = 4, 1 C of C$_{10}$(*C*H$_3$)$_8$P], 64.8 [d, $^2J_{\rm P-C}$ = 5, 1 C of *C*$_{10}$(CH$_3$)$_8$P], 69.4 [s, 1 C of *C*$_{10}$(CH$_3$)$_8$P], 133.6 [dd, $^1J_{\rm C-H}$ = 159, $^2J_{\rm P-C}$ = 20, 2 C of *C*$_6$H$_5$ (other phenyl resonances obscured by overlap with C$_6$D$_6$)], 137.9 [d, $^1J_{\rm P-C}$ =

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(26) Rahman, M. M.; Liu, H.-Y.; Eriks, K.; Prock, A.; Giering, W. P. *Organometallics* **1989**, *8*, 1−7.

(27) The coordination of PPh$_3$ is sufficiently weak that Cp*TaCl$_4$(PPh$_3$) is not spectroscopically detected.

(28) (a) McNally, J. P.; Leong, V. S.; Cooper, N. J. in *Experimental Organometallic Chemistry*; Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; chapter 2, pp 6−23. (b) Burger, B. J.; Bercaw, J. E. in *Experimental Organometallic Chemistry*; Wayda, A. L.; Darensbourg, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; chapter 4, pp 79−98. (c) Shriver, D. F.; Drezdzon, M. A.; *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley-Interscience: New York, 1986.

27, 1 C of $\mathit{C}_6\mathrm{H_5}$], 138.0 [d, $^{2}J_{\mathrm{P-C}} = 8$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 138.4 [s, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 141.0 [d, $^{2}J_{\mathrm{P-C}} = 11$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 144.7 [d, $^{3}J_{\mathrm{P-C}} = 3$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 147.3 [s, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 151.0 [d, $^{1}J_{\mathrm{P-C}} = 25$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 152.0 [s, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 155.2 [d, $^{1}J_{\mathrm{P-C}} = 15$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$]. ^{31}P NMR ($\mathrm{C_6D_6}$): −47.1 [s].

Synthesis of $\mathbf{Ph[(C_5Me_4)_2]PS}$. A mixture of $\mathrm{PhP[(C_5Me_4)_2]}$ (150 mg, 0.43 mmol) and sulfur (13 mg, 0.41 mmol) in toluene (10 mL) was stirred at room temperature for 1 h. After this period, the volatile components were removed from the mixture in vacuo, and the residue was washed with pentane (2 × 5 mL) and dried in vacuo to give $\mathrm{Ph[(C_5Me_4)_2]PS}$ as a pale brown solid (80 mg, 52%). Anal. calcd for $\mathrm{C_{24}H_{29}PS}$: C, 75.8%; H, 7.7%. Found: C, 73.9%; H, 7.4%. IR Data (KBr disk, cm^{-1}): 3071 (m), 3048 (m), 2959 (vs), 2921 (vs), 2859 (s), 1632 (m), 1583 (s), 1563 (s), 1478 (m), 1437 (vs), 1376 (s), 1322 (s), 1299 (m), 1275 (m), 1194 (s), 1176 (m), 1117 (s), 1096 (vs), 1076 (s), 1043 (m), 1026 (m), 1000 (m), 986 (m), 968 (w), 906 (w), 855 (w), 768 (m), 754 (vs), 744 (vs), 715 (vs), 691 (vs), 660 (s), 645 (vs), 614 (vs), 584 (s), 569 (m), 529 (s), 502 (vs), 494 (vs), 466 (s), 412 (m). ^{1}H NMR ($\mathrm{C_6D_6}$): 0.80 [s, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 1.22 [s, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 1.44 [s, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 1.53 [d, $^{4}J_{\mathrm{P-H}} = 3$, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 1.56 [s, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 1.71 [s, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 1.75 [s, 3 H of 2 $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 2.24 [d, $^{4}J_{\mathrm{P-H}} = 3$, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 7.09 [m, 1 H of $\mathrm{C_6\mathit{H}_5}$], 7.15 [m, 2 H of $\mathrm{C_6\mathit{H}_5}$], 8.34 [dd, $^{3}J_{\mathrm{P-H}} = 14.5$, $^{3}J_{\mathrm{H-H}} = 8$, 2 H of $\mathrm{C_6\mathit{H}_5}$]. ^{13}C NMR ($\mathrm{C_6D_6}$): 10.7 [q, $^{1}J_{\mathrm{C-H}} = 126$, 1 C of $\mathrm{C_{10}(\mathit{C}H_3)_8P}$], 10.8 [q, $^{1}J_{\mathrm{C-H}} = 126$, 1 C of $\mathrm{C_{10}(\mathit{C}H_3)_8P}$], 13.2 [q, $^{1}J_{\mathrm{C-H}} = 126$, 1 C of $\mathrm{C_{10}(\mathit{C}H_3)_8P}$], 13.3 [dq, $^{1}J_{\mathrm{C-H}} = 127$, $^{3}J_{\mathrm{P-C}} = 3$, 1 C of $\mathrm{C_{10}(\mathit{C}H_3)_8P}$], 13.5 [q, $^{1}J_{\mathrm{C-H}} = 126$, 1 C of $\mathrm{C_{10}(\mathit{C}H_3)_8P}$], 13.8 [dq, $^{1}J_{\mathrm{C-H}} = 127$, $^{4}J_{\mathrm{P-C}} = 4$, 1 C of $\mathrm{C_{10}(\mathit{C}H_3)_8P}$], 19.0 [q, $^{1}J_{\mathrm{C-H}} = 129$, 1 C of $\mathrm{C_{10}(\mathit{C}H_3)_8P}$], 19.1 [q, $^{1}J_{\mathrm{C-H}} = 128$, 1 C of $\mathrm{C_{10}(\mathit{C}H_3)_8P}$], 65.0 [d, $^{2}J_{\mathrm{P-C}} = 13$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 65.8 [d, $^{2}J_{\mathrm{P-C}} = 15$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 128.3 [dd, $^{1}J_{\mathrm{C-H}} = 159$, $^{3}J_{\mathrm{P-C}} = 9$, 2 C of $\mathit{C}_6\mathrm{H_5}$], 130.9 [dd, $^{1}J_{\mathrm{C-H}} = 159$, $^{4}J_{\mathrm{P-C}} = 3$, 1 C of $\mathit{C}_6\mathrm{H_5}$], 132.3 [dd, $^{1}J_{\mathrm{C-H}} = 162$, $^{2}J_{\mathrm{P-C}} = 13$, 2 C of $\mathit{C}_6\mathrm{H_5}$], 135.7 [dt, $^{2}J_{\mathrm{C-H}} = 7$, $^{1}J_{\mathrm{P-C}} = 84$, 1 C of $\mathit{C}_6\mathrm{H_5}$], 137.8 [d, $^{2}J_{\mathrm{P-C}} = 15$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 139.1 [d, $^{2}J_{\mathrm{P-C}} = 14$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 146.7 [d, $^{1}J_{\mathrm{P-C}} = 94$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 147.7 [d, $^{3}J_{\mathrm{P-C}} = 5$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 147.9 [d, $^{3}J_{\mathrm{P-C}} = 9$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 149.3 [d, $^{1}J_{\mathrm{P-C}} = 98$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 149.4 [d, $^{3}J_{\mathrm{P-C}} = 4$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 157.6 [d, $^{3}J_{\mathrm{P-C}} = 10$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$]. ^{31}P NMR ($\mathrm{C_6D_6}$): 11.1 [t, $^{3}J_{\mathrm{P-H}} = 14$].

Synthesis of Ph[*R*,*R*-$\mathbf{Me_2C_4H_6}$]PS. A mixture of PhP[*R*,*R*-$\mathrm{Me_2C_4H_6}$] (100 mg, 0.52 mmol) and sulfur (16 mg, 0.50 mmol) in toluene (10 mL) was stirred at room temperature for 1.5 h. After this period, the volatile components were removed from the mixture in vacuo giving an oily residue. The residue was dissolved in pentane (15 mL) and the solution was concentrated (to 1 mL) and cooled at 0 °C, thereby depositing a precipitate. The precipitate was isolated by filtration and dried in vacuo giving Ph[*R*,*R*-$\mathrm{Me_2C_4H_6}$]PS as a white cotton-like solid (100 mg, 86%). Anal. calcd For $\mathrm{C_{12}H_{17}PS}$: C, 64.3%; H, 7.6%. Found: C, 64.4%; H, 7.5%. IR Data (KBr disk, cm^{-1}): 3071 (m), 3049 (m), 2963 (s), 2924 (s), 2860 (s), 1478 (m), 1436 (vs), 1372 (m), 1310 (m), 1279 (m), 1249 (w), 1178 (w), 1160 (m), 1102 (vs), 1074 (s), 1052 (m), 1027 (m), 1000 (m), 986 (m), 924 (m), 849 (w), 819 (m), 752 (s), 698 (vs), 649 (vs), 576 (vs), 538 (m), 481 (s), 406 (w). ^{1}H NMR ($\mathrm{C_6D_6}$): 0.64 [dd, $^{3}J_{\mathrm{P-H}} = 17$, $^{3}J_{\mathrm{H-H}} = 7$, 3 H of 2 $\mathrm{C\mathit{H}_3}$], 0.89 [ddq, $J = 13, 5, 3$, 1 H of 2 $\mathrm{C\mathit{H}_2}$], 1.21 [dd, $^{3}J_{\mathrm{P-H}} = 18$, $^{3}J_{\mathrm{H-H}} = 7$, 3 H of 2 $\mathrm{C\mathit{H}_3}$], 1.33 [ddq, $J = 13, 5, 3$, 1 H of 2 $\mathrm{C\mathit{H}_2}$], 1.64 [m, 2 H of 2 $\mathrm{C\mathit{H}_2}$], 2.01 [m, 1 H of 2 $\mathrm{C\mathit{H}}$], 2.24 [m, 1 H of 2 $\mathrm{C\mathit{H}}$], 7.07 [m, 3 H of $\mathrm{C_6\mathit{H}_5}$], 7.81 [m, 2 H of $\mathrm{C_6\mathit{H}_5}$]. ^{13}C NMR ($\mathrm{CDCl_3}$): 13.9 [q, $^{1}J_{\mathrm{C-H}} = 128$, 1 C of 2 $\mathit{C}\mathrm{H_3}$], 14.6 [q, $^{1}J_{\mathrm{C-H}} = 129$, 1 C of 2 $\mathit{C}\mathrm{H_3}$], 33.5 [dt, $^{1}J_{\mathrm{C-H}} = 127$, $^{2}J_{\mathrm{P-C}} = 8$, 1 C of 2 $\mathit{C}\mathrm{H_2}$], 33.7 [dt, $^{1}J_{\mathrm{C-H}} = 127$, $^{2}J_{\mathrm{P-C}} = 7$, 1 C of 2 $\mathit{C}\mathrm{H_2}$], 35.6 [dd, $^{1}J_{\mathrm{C-H}} = 132$, $^{1}J_{\mathrm{P-C}} = 53$, 1 C of 2 $\mathit{C}\mathrm{H}$], 45.1 [dd, $^{1}J_{\mathrm{C-H}} = 130$, $^{1}J_{\mathrm{P-C}} = 53$, 1 C of 2 $\mathit{C}\mathrm{H}$], 128.3 [dd, $^{1}J_{\mathrm{C-H}} = 162$, $^{2}J_{\mathrm{P-C}} = 11$, 2 C of $\mathit{C}_6\mathrm{H_5}$], 130.3 [d, $^{1}J_{\mathrm{P-C}} = 65$, 1 C of $\mathit{C}_6\mathrm{H_5}$], 131.5 [dd, $^{1}J_{\mathrm{C-H}} = 161$, $^{4}J_{\mathrm{P-C}} = 3$, 1 C of $\mathit{C}_6\mathrm{H_5}$], 131.9 [dd, $^{1}J_{\mathrm{C-H}} = 161$, $^{3}J_{\mathrm{P-C}} = 9$, 2 C of $\mathit{C}_6\mathrm{H_5}$]. ^{31}P NMR ($\mathrm{C_6D_6}$): 66.1 [s].

Synthesis of $\mathbf{Ph[(C_5Me_4)_2]PSe}$. A mixture of $\mathrm{PhP[(C_5Me_4)_2]}$ (200 mg, 0.57 mmol) and selenium (50 mg, 0.63 mmol) in toluene (10 mL) was stirred at room temperature for 1 h. After this period, the mixture was filtered and the volatile components were removed from the filtrate in vacuo. The residue was washed with pentane (2 × 5 mL) and dried in vacuo to give $\mathrm{Ph[(C_5Me_4)_2]PSe}$ as a pale brown solid (180 mg, 73%). Anal. calcd For $\mathrm{C_{24}H_{29}PSe}$: C, 67.4%; H, 6.8%. Found: C, 67.8%; H, 6.7%. IR Data (KBr disk, cm^{-1}): 2968 (s), 2928 (vs), 2860 (s), 1632 (m), 1566 (vs), 1478 (m), 1436 (vs), 1379 (s), 1322 (s), 1276 (w), 1197 (m), 1177 (m), 1159 (w), 1118 (m), 1094 (vs), 1076 (m), 1041 (w), 1028 (m), 990 (m), 969 (w), 915 (vw), 858 (vw), 770 (m), 746 (vs), 706 (vs), 695 (vs), 660 (m), 632 (m), 619 (m), 601 (vs), 576 (s), 541 (vs), 497 (vs), 487 (s), 464 (m), 444 (m), 412 (w). ^{1}H NMR ($\mathrm{C_6D_6}$): 0.79 [s, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 1.23 [s, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 1.43 [s, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 1.54 [s, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 1.56 [d, $^{4}J_{\mathrm{P-H}} = 3$, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 1.73 [s, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 1.75 [s, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 2.23 [d, $^{4}J_{\mathrm{P-H}} = 3$, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 7.06 [m, 1 H of $\mathrm{C_6\mathit{H}_5}$], 7.12 [m, 2 H of $\mathrm{C_6\mathit{H}_5}$], 8.35 [dd, $^{3}J_{\mathrm{P-H}} = 15$, $^{3}J_{\mathrm{H-H}} = 7$, 2 H of $\mathrm{C_6\mathit{H}_5}$]. ^{13}C NMR ($\mathrm{C_6D_6}$): 10.7 [q, $^{1}J_{\mathrm{C-H}} = 126$, 1 C of $\mathrm{C_{10}(\mathit{C}H_3)_8P}$], 10.8 [q, $^{1}J_{\mathrm{C-H}} = 126$, 1 C of $\mathrm{C_{10}(\mathit{C}H_3)_8P}$], 13.1 [q, $^{1}J_{\mathrm{C-H}} = 126$, 1 C of $\mathrm{C_{10}(\mathit{C}H_3)_8P}$], 13.1 [dq, $^{1}J_{\mathrm{C-H}} = 125$, $^{3}J_{\mathrm{P-C}} = 5$, 1 C of $\mathrm{C_{10}(\mathit{C}H_3)_8P}$], 13.4 [q, $^{1}J_{\mathrm{C-H}} = 126$, 1 C of $\mathrm{C_{10}(\mathit{C}H_3)_8P}$], 14.1 [dq, $^{1}J_{\mathrm{C-H}} = 126$, $^{3}J_{\mathrm{P-C}} = 4$, 1 C of $\mathrm{C_{10}(\mathit{C}H_3)_8P}$], 19.2 [q, $^{1}J_{\mathrm{C-H}} = 128$, 1 C of $\mathrm{C_{10}(\mathit{C}H_3)_8P}$], 19.6 [q, $^{1}J_{\mathrm{C-H}} = 129$, 1 C of $\mathrm{C_{10}(\mathit{C}H_3)_8P}$], 65.7 [d, $^{2}J_{\mathrm{P-C}} = 15$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 65.9 [d, $^{2}J_{\mathrm{P-C}} = 12$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 131.0 [dd, $^{1}J_{\mathrm{C-H}} = 161$, $^{4}J_{\mathrm{P-C}} = 3$, 1 C of $\mathit{C}_6\mathrm{H_5}$], 132.7 [dd, $^{1}J_{\mathrm{C-H}} = 162$, $^{2}J_{\mathrm{P-C}} = 13$, 2 C of $\mathit{C}_6\mathrm{H_5}$], 134.4 [dt, $^{2}J_{\mathrm{C-H}} = 7$, $^{1}J_{\mathrm{P-C}} = 74$, 1 C of $\mathit{C}_6\mathrm{H_5}$ (other phenyl resonances obscured by overlap with $\mathrm{C_6D_6}$)], 137.9 [d, $^{2}J_{\mathrm{P-C}} = 15$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 139.2 [d, $^{2}J_{\mathrm{P-C}} = 15$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 144.4 [d, $^{1}J_{\mathrm{P-C}} = 87$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 147.6 [d, $^{1}J_{\mathrm{P-C}} = 89$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 147.9 [d, $^{3}J_{\mathrm{P-C}} = 8$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 148.0 [d, $^{3}J_{\mathrm{P-C}} = 5$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 149.5 [d, $^{3}J_{\mathrm{P-C}} = 4$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$], 158.2 [d, $^{3}J_{\mathrm{P-C}} = 10$, 1 C of $\mathit{C}_{10}\mathrm{(CH_3)_8P}$]. ^{31}P NMR ($\mathrm{C_6D_6}$): −7.3 [t, $^{3}J_{\mathrm{P-H}} = 14$, $^{1}J_{\mathrm{P-Se}} = 730$]. ^{77}Se NMR ($\mathrm{C_6D_6}$): −231 [d, $^{1}J_{\mathrm{Se-P}} = 730$].

Synthesis of Ph[*R*,*R*-$\mathbf{Me_2C_4H_6}$]PSe. A mixture of PhP[*R*,*R*-$\mathrm{Me_2C_4H_6}$] (100 mg, 0.52 mmol) and selenium powder (80 mg, 1.01 mmol) in toluene (10 mL) was stirred at room temperature for 2 h. After this period, the mixture was filtered, and the volatile components were removed from the filtrate in vacuo giving oily residue. The residue was dissolved in pentane (15 mL) and the solution was concentrated (to 1 mL) and cooled at 0 °C, thereby depositing a precipitate. The precipitate was isolated by filtration and dried in vacuo giving Ph[*R*,*R*-$\mathrm{Me_2C_4H_6}$]PSe as a white cotton-like solid (135 mg, 96%). Anal. calcd For $\mathrm{C_{12}H_{17}PSe}$: C, 53.2%; H, 6.3%. Found: C, 53.4%; H, 6.1%. IR Data (KBr disk, cm^{-1}): 3070 (m), 3046 (m), 2962 (s), 2922 (vs), 2857 (s), 1477 (m), 1435 (vs), 1372 (m), 1341 (w), 1310 (m), 1277 (m), 1249 (m), 1180 (w), 1156 (m), 1099 (vs), 1074 (s), 1051 (s), 1027 (m), 999 (s), 924 (m), 847 (w), 817 (m), 752 (vs), 697 (vs), 657 (vs), 642 (vs), 547 (vs), 526 (vs), 483 (s), 463 (s), 405 (m). ^{1}H NMR ($\mathrm{C_6D_6}$): 0.61 [dd, $^{3}J_{\mathrm{P-H}} = 18$, $^{3}J_{\mathrm{H-H}} = 7$, 3 H of 2 $\mathrm{C\mathit{H}_3}$], 0.87 [ddq, $J = 13, 5, 3$, 1 H of 2 $\mathrm{C\mathit{H}_2}$], 1.21 [dd, $^{3}J_{\mathrm{P-H}} = 19$, $^{3}J_{\mathrm{H-H}} = 7$, 3 H of 2 $\mathrm{C\mathit{H}_3}$], 1.29 [ddq, $J = 13, 5, 3$, 1 H of 2 $\mathrm{C\mathit{H}_2}$], 1.56 [m, 2 H of 2 $\mathrm{C\mathit{H}_2}$], 2.04 [m, 1 H of 2 $\mathrm{C\mathit{H}}$], 2.45 [m, 1 H of 2 $\mathrm{C\mathit{H}}$], 7.04 [m, 3 H of $\mathrm{C_6\mathit{H}_5}$], 7.84 [m, 2 H of $\mathrm{C_6\mathit{H}_5}$]. ^{13}C NMR ($\mathrm{CDCl_3}$): 14.0 [dq, $^{1}J_{\mathrm{C-H}} = 128$, $^{2}J_{\mathrm{P-C}} = 2$, 1 C of 2 $\mathit{C}\mathrm{H_3}$], 16.1 [q, $^{1}J_{\mathrm{C-H}} = 129$, 1 C of 2 $\mathit{C}\mathrm{H_3}$], 33.6 [dt, $^{1}J_{\mathrm{C-H}} = 131$, $^{2}J_{\mathrm{P-C}} = 8$, 1 C of 2 $\mathit{C}\mathrm{H_2}$], 34.5 [dt, $^{1}J_{\mathrm{C-H}} = 131$, $^{2}J_{\mathrm{P-C}} = 6$, 1 C of 2 $\mathit{C}\mathrm{H_2}$], 35.3 [dd, $^{1}J_{\mathrm{C-H}} = 127$, $^{1}J_{\mathrm{P-C}} = 46$, 1 C of 2 $\mathit{C}\mathrm{H}$], 46.1 [dd, $^{1}J_{\mathrm{C-H}} = 130$, $^{1}J_{\mathrm{P-C}} = 48$, 1 C of 2 $\mathit{C}\mathrm{H}$], 128.3 [dd, $^{1}J_{\mathrm{C-H}} = 161$, $^{2}J_{\mathrm{P-C}} = 11$, 2 C of $\mathit{C}_6\mathrm{H_5}$], 128.7 [d, $^{1}J_{\mathrm{P-C}} = 57$, 1 C of $\mathit{C}_6\mathrm{H_5}$], 131.6 [dd, $^{1}J_{\mathrm{C-H}} = 163$, $^{4}J_{\mathrm{P-C}} = 3$, 1 C of $\mathit{C}_6\mathrm{H_5}$], 132.7 [dd, $^{1}J_{\mathrm{C-H}} = 161$, $^{3}J_{\mathrm{P-C}} = 9$, 2 C of $\mathit{C}_6\mathrm{H_5}$]. ^{31}P NMR ($\mathrm{C_6D_6}$): 58.9 [s, $^{1}J_{\mathrm{P-Se}} = 747$]. ^{77}Se NMR ($\mathrm{C_6D_6}$): −394 [d, $^{1}J_{\mathrm{P-Se}} = 747$].

Preparation of $\mathbf{Cp^{*}TaCl_4\{PhP[(C_5Me_4)_2]\}}$. A mixture of $\mathrm{Cp^{*}TaCl_4}$ (15 mg, 0.04 mmol) and $\mathrm{PhP[(C_5Me_4)_2]}$ (10 mg, 0.03 mmol) was treated with benzene (1 mL), resulting in the immediate formation of an orange-yellow solution. After 30 min, the solution was filtered and the volatile components were removed from the filtrate in vacuo to give $\mathrm{Cp^{*}TaCl_4\{PhP[(C_5Me_4)_2]\}}$ as an orange-yellow solid. ^{1}H NMR ($\mathrm{C_6D_6}$): 0.61 [s, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 1.16 [s, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 1.59 [s, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 1.65 [s, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 1.81 [s, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 1.82 [s, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 2.21 [s, 15 H of $\mathrm{C_5(C\mathit{H}_3)_5}$], 2.47 [s, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 2.49 [d, $^{4}J_{\mathrm{P-H}} = 2$, 3 H of $\mathrm{C_{10}(C\mathit{H}_3)_8P}$], 6.98 [td, $^{5}J_{\mathrm{P-H}} = 2$, $^{3}J_{\mathrm{H-H}} = 7$, 1 H of $\mathrm{C_6\mathit{H}_5}$], 7.15 [td, $^{4}J_{\mathrm{P-H}} = 2$, $^{3}J_{\mathrm{H-H}} = 8$, 2 H of $\mathrm{C_6\mathit{H}_5}$], 8.15 [t, $^{5}J_{\mathrm{P-H}} = {}^{3}J_{\mathrm{H-H}} = 8$, 2 H of $\mathrm{C_6\mathit{H}_5}$]. ^{31}P NMR ($\mathrm{C_6D_6}$): −9.1 [br. s].

Preparation of $\mathbf{Cp^{*}TaCl_4\{PhP[}$*R*,*R*-$\mathbf{Me_2C_4H_6]\}}$. A mixture of $\mathrm{Cp^{*}TaCl_4}$ (15 mg, 0.04 mmol) and PhP[*R*,*R*-$\mathrm{Me_2C_4H_6}$] (10 mg, 0.052

mmol) was treated with benzene (1 mL) giving immediately an orange-yellow solution. After 30 min, the solution was filtered and the volatile components were removed from the filtrate in vacuo, and the residue was washed with pentane (1 mL) to give Cp*TaCl$_4${PhP[*R*,*R*-Me$_2$C$_4$H$_6$]} as an orange-yellow solid. ^{1}H NMR (C$_6$D$_6$): 1.06 [m, 1H of 2 C*H*$_2$], 1.47 [dd, $^3J_{\mathrm{H-H}} = 7$, $^3J_{\mathrm{P-H}} = 12$, 3 H of 2 C*H*$_3$], 1.76 [dd, $^3J_{\mathrm{H-H}} = 7$, $^3J_{\mathrm{P-H}} = 13$, 3 H of 2 C*H*$_3$], 1.82 [m, 2 H of 2 C*H*$_2$], 1.92 [m, 1 H of 2 C*H*$_2$], 2.21 [s, 15 H of C$_5$(C*H*$_3$)$_5$], 3.01 [br. s, 1 H of 2 C*H*], 3.48 [m, 1 H of 2 C*H*], 7.04 [t, $^3J_{\mathrm{H-H}} = 7$, 1 H of C$_6$*H*$_5$], 7.13 [t, $^3J_{\mathrm{H-H}} = 7$, 2 H of C$_6$*H*$_5$], 7.75 [t, $^3J_{\mathrm{H-H}} = {}^3J_{\mathrm{P-H}} = 7$, 2 H of C$_6$*H*$_5$]. ^{31}P NMR (C$_6D_6$): 27.6 [s].

Preparation of Cp*MoCl$_4${PhP[(C$_5$Me$_4$)$_2$]}. A mixture of Cp*MoCl$_4$ (15 mg, 0.04 mmol) and PhP[(C$_5$Me$_4$)$_2$] (10 mg, 0.03 mmol) in benzene (1 mL) was allowed to stand at room-temperature overnight. After this period, the volatile components were removed in vacuo. The residue was extracted into pentane (3 mL) and filtered. The volatile components were removed from the filtrate in vacuo to give Cp*MoCl$_4${PhP[(C$_5$Me$_4$)$_2$]} as a purple solid.

Synthesis of *trans*-Ir{P[(C$_5$Me$_4$)$_2$]Ph}$_2$(CO)Cl. A mixture of [(COD)Ir(μ-Cl)]$_2$ (105 mg, 0.16 mmol) and PhP[(C$_5$Me$_4$)$_2$] (230 mg, 0.66 mmol) in toluene (20 mL) was stirred at room temperature for 30 min to give an orange solution which was treated with CO (1 atm) and stirred at room-temperature overnight to give a yellow solution. After this period, the volatile components were removed in vacuo to yield a yellow residue that was washed with pentane (2 × 10 mL) and dried to give yellow Ir{P[(C$_5$Me$_4$)$_2$]Ph}$_2$(CO)Cl as a 1:1 mixture of {*R*/*R*, *S*/*S*} and *R*/*S* diasteromers (270 mg, 91%). Anal. calcd for C$_{49}$H$_{58}$OP$_2$ClIr: C, 61.8%; H, 6.1%. Found: C, 62.2%; H, 6.7%. IR Data (KBr disk, cm^{-1}): 3054 (w), 2964 (s), 2921 (s), 2860 (m), 2732 (w), 1953 (vs) [ν(CO)], 1638 (w), 1570 (m), 1480 (w), 1435 (s), 1375 (m), 1321 (w), 1277 (w), 1197 (w), 1124 (w), 1092 (m), 1076 (m), 1026 (w), 985 (w), 852 (vw), 766 (w), 740 (s), 701 (s), 658 (w), 632 (vw), 618 (w), 599 (s), 573 (w), 510 (s), 486 (m), 458 (w). ν(CO): 1955 (Nujol), 1960 (pentane). ^{1}H NMR (C$_6$D$_6$): 0.79 [d, $^4J_{\mathrm{P-H}} = 3$, 6 H of 2 C$_{10}$(C*H*$_3$)$_8$P], 1.20 [d, $^4J_{\mathrm{P-H}} = 3$, 6 H of 2 C$_{10}$(C*H*$_3$)$_8$P], 1.53 [s, 6 H of 2 C$_{10}$(C*H*$_3$)$_8$P], 1.64 [s, 6 H of 2 C$_{10}$(C*H*$_3$)$_8$P], 1.79 [s, 6 H of 2 C$_{10}$(C*H*$_3$)$_8$P], 1.81 [s, 6 H of 2 C$_{10}$(C*H*$_3$)$_8$P], 2.19 [d, $^4J_{\mathrm{P-H}} = 2$, 6 H of 2 C$_{10}$(C*H*$_3$)$_8$P], 2.61 [s, 6 H of 2 C$_{10}$(C*H*$_3$)$_8$P], 7.04 [t, $^3J_{\mathrm{H-H}} = 7$, 2 H of 2 C$_6$*H*$_5$], 7.17 [dt, $^3J_{\mathrm{H-H}} = 8$, $^4J_{\mathrm{P-H}} = 4$, 4 H of 2 C$_6$*H*$_5$], 8.23 [m, 4 H of 2 C$_6$*H*$_5$]. ^{13}C NMR (C$_6$D$_6$): 11.1 [q, $^1J_{\mathrm{C-H}} = 126$, 2 C of 2 C$_{10}$(*C*H$_3$)$_8$P], 11.2 [q, $^1J_{\mathrm{C-H}} = 126$, 2 C of 2 C$_{10}$(*C*H$_3$)$_8$P], 13.3 [q, $^1J_{\mathrm{C-H}} = 125$, 4 C of 2 C$_{10}$(*C*H$_3$)$_8$P], 15.0 [q, $^1J_{\mathrm{C-H}} = 127$, 2 C of 2 C$_{10}$(*C*H$_3$)$_8$P], 15.8 [dq, $^1J_{\mathrm{C-H}} = 125$, $^3J_{\mathrm{P-C}} = 5$, 2 C of 2 C$_{10}$(*C*H$_3$)$_8$P], 19.9 [q, $^1J_{\mathrm{C-H}} = 129$, 1 C of 2 C$_{10}$(*C*H$_3$)$_8$P], 20.0 [q, $^1J_{\mathrm{C-H}} = 129$, 1 C of 2 C$_{10}$(*C*H$_3$)$_8$P], 20.1 [q, $^1J_{\mathrm{C-H}} = 129$, 1 C of 2 C$_{10}$(*C*H$_3$)$_8$P], 20.1 [q, $^1J_{\mathrm{C-H}} = 129$, 1 C of 2 C$_{10}$(*C*H$_3$)$_8$P], 65.5 [s, 2 C of 2 C$_{10}$(*C*H$_3$)$_8$P], 67.8 [s, 2 C of 2 C$_{10}$(*C*H$_3$)$_8$P], 127.6 [d, $^1J_{\mathrm{C-H}} = 156$, 2 C of *C*$_6$H$_5$], 129.3 [d, $^1J_{\mathrm{C-H}} = 160$, 1 C of *C*$_6$H$_5$], 134.0 [dt, $^1J_{\mathrm{C-H}} = 160$, $^2J_{\mathrm{P-C}} = 7$, 1 C of *C*$_6$H$_5$], 134.1 [dt, $^1J_{\mathrm{C-H}} = 161$, $^2J_{\mathrm{P-C}} = 7$, 1 C of *C*$_6$H$_5$], 135.6 [t, $^1J_{\mathrm{P-C}} = 25$, 1 C of *C*$_6$H$_5$], 138.4 [t, $^3J_{\mathrm{P-C}} = 6$, 2 C of 2 *C*$_{10}$(CH$_3$)$_8$P], 138.7 [t, $^3J_{\mathrm{P-C}} = 5$, 2 C of 2 *C*$_{10}$(CH$_3$)$_8$P], 145.6 [t, $^2J_{\mathrm{P-C}} = 31$, *C*O], 145.7 [t, $^2J_{\mathrm{P-C}} = 31$, *C*O], 147.2 [d, $^2J_{\mathrm{P-C}} = 10$, 2 C of 2 *C*$_{10}$(CH$_3$)$_8$P], 147.3 [t, $^3J_{\mathrm{P-C}} = 5$, 1 C of 2 *C*$_{10}$(CH$_3$)$_8$P], 147.4 [t, $^3J_{\mathrm{P-C}} = 5$, 1 C of 2 *C*$_{10}$(CH$_3$)$_8$P], 148.3 [d, $^1J_{\mathrm{P-C}} = 58$, 2 C of 2 *C*$_{10}$(CH$_3$)$_8$P], 148.3 [s, 2 C of 2 *C*$_{10}$(CH$_3$)$_8$P], 148.3 [d, $^1J_{\mathrm{P-C}} = 58$, 2 C of 2 *C*$_{10}$(CH$_3$)$_8$P], 154.4 [t, $^2J_{\mathrm{P-C}} = 7$, 2 C of 2 *C*$_{10}$(CH$_3$)$_8$P]. ^{31}P NMR (C$_6$D$_6$): −14.9 [t, $^3J_{\mathrm{P-H}} = 5$], −15.2 [t, $^3J_{\mathrm{P-H}} = 5$] (the two signals correspond to the 1:1 mixture of {*R*/*R*, *S*/*S*} and *R*/*S* diasteromers).

Synthesis of *trans*-Ir{PPh[(*R*,*R*)-Me$_2$C$_4$H$_6$]}$_2$(CO)Cl. A mixture of [(COD)Ir(μ-Cl)]$_2$ (720 mg, 1.07 mmol) and PhP[(*R*,*R*)-Me$_2$C$_4$H$_6$] (900 mg, 4.73 mmol) in toluene (50 mL) was stirred at room temperature for 1 h to give an orange solution. The orange solution was treated with CO (1 atm) and stirred at room-temperature overnight and then heated at 80 °C for 2 h to give a yellow solution. After this period, the solution was filtered, and the volatile components were removed from the filtrate in vacuo. The yellow residue was washed with pentane (3 × 10 mL) and dried in vacuo to give *trans*-Ir{PPh[(*R*,*R*)-Me$_2$C$_4$H$_6$]}$_2$(CO)Cl as a bright yellow solid (1.3 g, 95%). Anal. calcd for C$_{25}$H$_{34}$OP$_2$ClIr: C, 46.9%; H, 5.4%. Found: C, 46.9%; H, 5.2%. IR Data (KBr disk, cm^{-1}): 3078 (m), 3054 (m), 2952 (s), 2924 (s), 2860 (s), 1937 (vs) [ν(CO)], 1481 (m), 1446 (s), 1432 (s), 1376 (m), 1308 (w), 1275 (w), 1249 (m), 1183 (m), 1157 (m), 1101 (s), 1074 (m), 1050 (m), 1027 (w), 1005 (m), 940 (w), 919 (w), 845 (w), 816 (w), 747 (s), 696 (s), 637 (vs), 599 (m), 546 (s), 517 (vs), 474 (m). ν(CO): 1937 (in Nujol), 1957 (in pentane). ^{1}H NMR (C$_6$D$_6$): 0.85 [q, $^3J_{\mathrm{H-H}} = {}^3J_{\mathrm{P-H}} = 7$, 3 H of 2 C*H*$_3$], 1.14 [m, 1 H of 2 C*H*$_2$], 1.40 [m, 1 H of 2 C*H*$_2$], 1.69 [q, $^3J_{\mathrm{H-H}} = {}^3J_{\mathrm{P-H}} = 8$, 3 H of 2 C*H*$_3$], 1.71 [m, 1 H of 2 C*H*$_2$], 1.90 [m, 1 H of 2 C*H*$_2$], 2.84 [m, 1 H of 2 C*H*], 3.32 [m, 1 H of 2 C*H*], 7.07 [t, $^3J_{\mathrm{H-H}} = 8$, 1 H of C$_6$*H*$_5$], 7.15 [t, $^3J_{\mathrm{H-H}} = 8$, 2 H of C$_6$*H*$_5$], 7.93 [m, 2 H of C$_6$*H*$_5$]. ^{13}C NMR (CDCl$_3$): 14.9 [q, $^1J_{\mathrm{C-H}} = 126$, 1 C of 2 *C*H$_3$], 21.4 [tq, $^1J_{\mathrm{C-H}} = 128$, $^2J_{\mathrm{P-C}} = 5$, 1 C of 2 *C*H$_3$], 33.3 [dt, $^1J_{\mathrm{C-H}} = 135$, $^1J_{\mathrm{P-C}} = 16$, 1 C of 2 *C*H], 34.5 [dt, $^1J_{\mathrm{C-H}} = 135$, $^1J_{\mathrm{P-C}} = 17$, 1 C of 2 *C*H], 35.0 [dd, $^1J_{\mathrm{C-H}} = 130$, 1 C of 2 *C*H$_2$], 35.5 [t, $^1J_{\mathrm{C-H}} = 130$, 1 C of 2 *C*H$_2$], 127.7 [dt, $^1J_{\mathrm{C-H}} = 159$, $^3J_{\mathrm{P-C}} = 5$, 2 C of *C*$_6$H$_5$], 130.0 [d, $^1J_{\mathrm{C-H}} = 161$, 1 C of *C*$_6$H$_5$], 132.3 [t, $^1J_{\mathrm{P-C}} = 41$, 1 C of *C*$_6$H$_5$], 134.6 [dt, $^1J_{\mathrm{C-H}} = 166$, $^2J_{\mathrm{P-C}} = 11$, 2 C of *C*$_6$H$_5$], (*C*O not located). ^{31}P NMR (C$_6$D$_6$): 42.8 [s].

Synthesis of *trans*-Ir{Ph[*R*,*R*-Me$_2$C$_4$H$_6$]}$_2$(CO)Me. A suspension of Ir{Ph[*R*,*R*-Me$_2$C$_4$H$_6$]}$_2$(CO)Cl (200 mg, 0.31 mmol) in Et$_2$O (20 mL) was treated with MeLi (0.30 mL, 1.4 M solution in ether) at room temperature for 1 h giving orange-yellow suspension. After this period, the volatile components were removed from the mixture in vacuo, and the residue was extracted into pentane (100 mL), filtered, concentrated (to 1 mL) and filtered. The yellow residue was dried in vacuo to give Ir{Ph[*R*,*R*-Me$_2$C$_4$H$_6$]}$_2$(CO)Me as a yellow solid (130 mg, 67% yield). Anal. calcd For C$_{26}$H$_{37}$OP$_2$Ir: C, 50.4%; H, 6.0%. Found: C, 50.3%; H, 6.0%. IR Data (KBr disk, cm^{-1}): 2923 (s), 2861 (s), 1916 (vs) [ν(CO)], 1481 (m), 1446 (s), 1432 (s), 1374 (m), 1309 (w), 1273 (w), 1249 (w), 1183 (w), 1157 (w), 1100 (s), 1073 (m), 1050 (w), 1026 (w), 1003 (m), 939 (w), 918 (w), 848 (vw), 814 (w), 748 (s), 698 (s), 475 (m), 455 (m), 410 (w). ν(CO): 1933 (in pentane). ^{1}H NMR (C$_6$D$_6$): 0.26 [t, $^3J_{\mathrm{P-H}} = 9$, Ir−C*H*$_3$], 0.94 [q, $^3J_{\mathrm{H-H}} = {}^3J_{\mathrm{P-H}} = 7$, 3 H of 2 C*H*$_3$], 1.22 [m, 1 H of 2 C*H*$_2$], 1.33 [m, 1 H of 2 C*H*$_2$], 1.49 [q, $^3J_{\mathrm{H-H}} = {}^3J_{\mathrm{P-H}} = 8$, 3 H of 2 C*H*$_3$], 1.67 [m, 1 H of 2 C*H*$_2$], 2.00 [m, 1 H of 2 C*H*$_2$], 2.80 [m, 2 H of 2 C*H*], 7.07 [t, $^3J_{\mathrm{H-H}} = 7$, 1 H of C$_6$*H*$_5$], 7.15 [t, $^3J_{\mathrm{H-H}} = 7$, 2 H of C$_6$*H*$_5$], 7.87 [m, 2 H of C$_6$*H*$_5$]. ^{13}C NMR (C$_6$D$_6$): 1.4 [tq, $^1J_{\mathrm{C-H}} = 120$, $^2J_{\mathrm{P-C}} = 11$, Ir−*C*H$_3$], 14.2 [q, $^1J_{\mathrm{C-H}} = 127$, 1 C of 2 *C*H$_3$], 22.0 [tq, $^1J_{\mathrm{C-H}} = 127$, $^2J_{\mathrm{P-C}} = 5$, 1 C of 2 *C*H$_3$], 32.6 [dt, $^1J_{\mathrm{C-H}} = 129$, $^1J_{\mathrm{P-C}} = 16$, 1 C of 2 *C*H], 35.1 [t, $^1J_{\mathrm{C-H}} = 129$, 1 C of 2 *C*H$_2$], 35.6 [t, $^1J_{\mathrm{C-H}} = 128$, 1 C of 2 *C*H$_2$], 37.6 [dt, $^1J_{\mathrm{C-H}} = 132$, $^1J_{\mathrm{P-C}} = 16$, 1 C of 2 *C*H], 127.5 [dt, $^1J_{\mathrm{C-H}} = 167$, $^3J_{\mathrm{P-C}} = 5$, 2 C of *C*$_6$H$_5$], 129.6 [d, $^1J_{\mathrm{C-H}} = 160$, 1 C of *C*$_6$H$_5$], 134.0 [t, $^1J_{\mathrm{P-C}} = 19$, 1 C of *C*$_6$H$_5$], 135.1 [dt, $^1J_{\mathrm{C-H}} = 160$, $^2J_{\mathrm{P-C}} = 6$, 2 C of *C*$_6$H$_5$], *C*O [not located]. ^{31}P NMR (C$_6$D$_6$): 48.4 [s].

Synthesis of Ir{PPh[*R*,*R*-Me$_2$C$_4$H$_6$]}(COD)Cl. A mixture of [(COD)Ir(μ-Cl)]$_2$ (10 mg, 0.015 mmol) and PhP[*R*,*R*-Me$_2$C$_4$H$_6$] (10 mg, 0.052 mmol) in benzene (1 mL) was left at room-temperature overnight. After this period, the volatile components were removed from the mixture in vacuo, and the residue was washed with pentane (1 mL) to give Ir{PPh[*R*,*R*-Me$_2$C$_4$H$_6$]}(COD)Cl as a yellow-orange solid. ^{1}H NMR (C$_6$D$_6$): 0.75 [dd, $^3J_{\mathrm{P-H}} = 14$, $^3J_{\mathrm{H-H}} = 7$, 3 H of 2 C*H*$_3$], 0.91 [m, 1 H of 2 C*H*$_2$], 1.35 [m, 2 H of 2 C*H*$_2$], 1.48 [br s, 1 H of COD], 1.5−1.7 [m, 1 H of 2 C*H*$_2$ and 2 H of COD], 1.63 [dd, $^3J_{\mathrm{P-H}} = 18$, $^3J_{\mathrm{H-H}} = 7$, 3 H of 2 C*H*$_3$], 1.79 [m, 1 H of 2 C*H*$_2$], 1.97 [br s, 2 H of COD], 2.13 [br s, 2 H of COD], 2.65 [m, 1 H of 2 C*H*], 2.71 [br s, 1 H of COD],], 2.93 [br s, 2 H of COD],], 5.36 [br s, 2 H of COD], 6.98−7.09 [m, 3 H of C$_6$*H*$_5$], 7.44 [t, $^3J_{\mathrm{H-H}} = 8$, 2 H of C$_6$H$_5$]. ^{31}P NMR (C$_6$D$_6$): 34.3 [s].

Synthesis of Pd{P[*R*,*R*-Me$_2$C$_4$H$_6$]Ph}[η^2−*S*-C$_6$H$_4$C(H)(Me)-NMe$_2$]Cl. A mixture of Pd{[η^2-*S*-C$_6$H$_4$C(H)(Me)NMe$_2$]Cl}$_2$ (15 mg, 0.026 mmol) and PhP[*R*,*R*-Me$_2$C$_4$H$_6$] (10 mg, 0.052 mmol) in C$_6$D$_6$ (1 mL) was kept in an NMR tube at room temperature for 30 min. After this period, the volatile components were removed from the mixture in vacuo, and the residue was washed with pentane (1 mL) to give Pd{P[R,R-Me2C4H6]Ph}[η^2-*S*-C$_6$H$_4$C(H)(Me)NMe$_2$]Cl as a pale brown solid. ^{1}H NMR (C$_6$D$_6$): 0.89 [dd, $^3J_{\mathrm{P-H}} = 16$, $^3J_{\mathrm{H-H}} = 7$, 3 H of 2 C*H*$_3$], 1.15 [m, 1 H of 2 C*H*$_2$], 1.39 [m, 1 H of 2 C*H*$_2$], 1.40 [d, $^3J_{\mathrm{H-H}} = 7$, 3 H of CH(C*H*$_3$)N(CH$_3$)$_2$], 1.60 [m, 1 H of 2 C*H*$_2$], 1.61 [dd, $^3J_{\mathrm{P-H}} = 20$, $^3J_{\mathrm{H-H}} = 7$, 3 H of 2 C*H*$_3$], 1.94 [m, 1 H of 2 C*H*$_2$], 2.56 [d, $^4J_{\mathrm{H-H}} = 2$, 3 H of CH(CH$_3$)N(C*H*$_3$)$_2$], 2.60 [d, $^4J_{\mathrm{H-H}} = 3$, 3 H of CH(CH$_3$)N(C*H*$_3$)$_2$], 2.62 [m, 1 H of 2 C*H*], 3.22 [m, 1 H of C*H*(CH$_3$)-N(CH$_3$)$_2$], 3.90 [m, 1 H of 2 C*H*], 6.59 [t, $^3J_{\mathrm{H-H}} = 7$, 1 H of C$_6$*H*$_4$-

Table 4. Crystal, Intensity, Collection, and Refinement Data

	$PhP[(C_5Me_4)_2]$	$Ph[(C_5Me_4)_2]PS$	$Ph[(C_5Me_4)_2]PSe$	$Cp^*MoCl_4\{P[(C_5Me_4)_2]Ph\}$
lattice	orthorhombic	monoclinic	monoclinic	monoclinic
formula	$C_{24}H_{29}P$	$C_{24}H_{29}PS$	$C_{24}H_{29}PSe$	$C_{34}H_{44}Cl_4MoP$
formula weight	348.44	380.50	427.40	721.40
space group	$Pna2_1$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	14.043(1)	16.022(2)	16.250(4)	12.236(12)
b/Å	8.804(1)	7.391(1)	7.503(2)	14.601(15)
c/Å	16.407(2)	19.181(2)	19.078(4)	16.572(16)
α/deg	90	90	90	90
β/deg	90	112.27(1)	111.95(1)	99.93(2)
γ/deg	90	90	90	90
V/Å^3	2028.4(4)	2101.9(3)	2157.4(9)	2916(5)
Z	4	4	4	4
temperature (K)	223	238	238	233
radiation (λ, Å)	0.71073	0.71073	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.141	1.202	1.316	1.643
μ (Mo Kα), mm^{-1}	0.139	0.235	1.820	0.897
θ max, deg	28.3	28.3	28.4	28.9
no. of data	3893	4699	4779	7070
no. of parameters	236	244	244	374
R1	0.0521	0.0393	0.0430	0.0646
wR2	0.0952	0.1144	0.0941	0.1278
GOF	1.087	1.053	1.093	1.015
abs. struct. param.	0.06(12)	NA	NA	NA

	$Cp^*TaCl_4\{P[(C_5Me_4)_2]Ph\}$	$Ir\{P[(C_5Me_4)_2]Ph\}_2(CO)Cl$	$Ph[R,R\text{-}Me_2C_4H_6]PO$	$Ph[R,R\text{-}Me_2C_4H_6]PS$
lattice	triclinic	triclinic	monoclinic	triclinic
formula	$C_{34}H_{44}Cl_4T_aP$	$C_{49}H_{58}ClIrOP_2$	$C_{12}H_{17}PO$	$C_{12}H_{17}PS$
formula weight	806.41	952.54	208.23	224.29
space group	$P\bar{1}$	$P\bar{1}$	$P2_1$	$P\bar{1}$
a/Å	9.924(2)	11.967(2)	6.392(7)	7.166(1)
b/Å	17.206(3)	13.805(2)	7.497(8)	9.100(2)
c/Å	21.312(4)	14.918(2)	12.274(10)	10.080(2)
α/deg	104.329(3)	92.172(4)	90	75.803(4)
β/deg	99.530(3)	102.033(3)	100.71(2)	84.522(3)
γ/deg	100.223(4)	113.022(2)	90	83.910(4)
V/Å^3	3384.8(10)	2198.8(5)	577.9(12)	632.1(2)
Z	4	2	2	2
temperature (K)	238	233	233	233
radiation (λ, Å)	0.71073	0.71073	0.71073	0.71073
ρ (calcd.), g cm^{-3}	1.582	1.439	1.197	1.178
μ (Mo Kα), mm^{-1}	3.633	3.204	0.205	0.345
θ max, deg.	28.4	28.4	28.2	28.2
no. of data	14936	9553	2335	3357
no. of parameters	748	582	131	259
R1	0.0317	0.0549	0.0518	0.0486
wR2	0.0676	0.0946	0.0885	0.0954
GOF	1.015	1.022	1.023	1.045
abs. struct. param.	NA	NA	0.18(15)	0.00(13)

	$Ir\{Ph[R,R\text{-}Me_2C_4H_6]\}_2\text{-}(CO)Cl$	$Ir\{Ph[R,R\text{-}Me_2C_4H_6]\}_2\text{-}(CO)Me$	$Ir\{PPh[R,R\text{-}Me_2C_4H_6]\}\text{-}(COD)(Cl)$	$Pd\{P[R,R\text{-}Me_2C_4H_6]Ph)\}$ $[S\text{-}\eta^2\text{-}C_6H_4C(H)(Me)\text{-}N{-}Me_2]Cl$	$S,S\text{-}Me_2C_4H_6\text{-}(O_2SO_2)$
lattice	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic
formula	$C_{25}H_{34}ClIrOP_2$	$C_{26}H_{37}IrOP_2$	$C_{20}H_{29}ClIrP$	$C_{22}H_{31}ClNPPd$	$C_6H_{12}O_4S$
formula weight	640.11	619.70	528.05	482.30	180.22
space group	$P2_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a/Å	9.244(5)	9.1715(6)	9.8883(4)	9.261(2)	6.515(3)
b/Å	14.891(9)	14.780(1)	13.9564(7)	11.872(2)	11.386(5)
c/Å	9.648(5)	9.7107(6)	14.3346(7)	20.943(4)	11.817(4)
α/deg	90	90	90	90	90
β/deg	100.88(1)	101.541(1)	90	90	90
γ/deg	90	90	90	90	90
V/Å^3	1304(1)	1289.7(2)	1978.3(2)	2302.7(8)	876.5(6)
Z	2	2	4	4	4
temperature (K)	233	233	233	233	238
radiation (λ, Å)	0.71073	0.71073	0.71073	0.71073	0.71073
ρ (calcd), g cm^{-3}	1.630	1.596	1.773	1.391	1.366
μ (Mo Kα), mm^{-1}	5.358	5.315	6.963	0.997	0.337
θ max, deg.	28.2	28.2	28.3	28.3	28.3
no. of data	5190	5392	4553	5179	1984
no. of parameters	288	277	211	241	104
R1	0.0364	0.0210	0.0225	0.0165	0.0346
wR2	0.0991	0.0534	0.0538	0.0438	0.0736
GOF	1.095	1.027	1.044	1.039	1.050
abs struct param	0.01(1)	0.000(7)	−0.013(7)	0.00(2)	0.05(8)

$CH(CH_3)N(CH_3)_2]$, 6.65 [t, $^3J_{H-H} = {}^4J_{P-H} = 7$, 1 H of $C_6H_4CH(CH_3)N(CH_3)_2]$, 6.71 [d, $^3J_{H-H} = 7$, 1 H of $C_6H_4CH(CH_3)N(CH_3)_2]$, 6.80 [t, $^3J_{H-H} = 7$, 1 H of $C_6H_4CH(CH_3)N(CH_3)_2]$, 6.94 [m, 3 H of C_6H_5P], 7.65 [m, 2 H of C_6H_5P]. ^{31}P NMR (C_6D_6): 66.8 [s].

Synthesis of $CpFe(CO)\{PhP[(C_5Me_4)_2]\}Me$. (a) A mixture of $CpFe(CO)_2Me$ (ca. 10 mg) and $PhP[(C_5Me_4)_2]$ (ca.20 mg) in C_6D_6 (1 mL) was heated at 80 °C for 5 days. After this period, the volatile components were removed from the mixture in vacuo, and the residue was extracted into pentane (2 mL) and filtered. The pentane was removed from the filtrate to give $CpFe(CO)\{PhP[(C_5Me_4)_2]\}Me$ as a brown solid. IR Data (cyclohexane, cm^{-1}): 1921 (s). ^1H NMR (C_6D_6):[29] 0.23 [d, $^3J_{P-H} = 8$ Hz, $Fe-CH_3$], 0.48 [d, $^3J_{P-H} = 8$ Hz, $Fe-CH_3$], 4.19 [d, $^3J_{P-H} = 1$ Hz, C_5H_5], 4.30 [d, $^3J_{P-H} = 1$ Hz, C_5H_5]. $^{31}P\{^1H\}$ NMR (C_6D_6): 37.5 (s), 44.8 (s). (b) A mixture of $CpFe(CO)_2Me$ (ca. 10 mg) and $PhP[(C_5Me_4)_2]$ (ca.20 mg) in C_6D_6 (1 mL) was photolyzed for 5 h. After this period, the volatile components were removed from the mixture in vacuo, and the residue was extracted into pentane (2 mL) and filtered, and pentane was removed from the filtrate to give $CpFe(CO)(PhP[(C_5Me_4)_2])Me$ as a brown solid.

Synthesis of $CpFe(CO)\{P[R,R\text{-}Me_2C_4H_6]Ph\}Me$. (a) Preparation via $CpFe(CO)\{P[R,R\text{-}Me_2C_4H_6]Ph\}I$. A mixture of $CpFe(CO)_2I$ (ca. 10 mg) and $PhP[R,R\text{-}Me_2C_4H_6]$ (ca.10 mg) in C_6D_6 (1 mL) was heated at 80 °C overnight giving a green solution. After this period, the volatile components were removed from the solution in vacuo, and the residue was extracted into benzene (1 mL) and filtered. The benzene was removed from the filtrate and the residue was washed with pentane (1 mL) to give $CpFe(CO)\{P[R,R\text{-}Me_2C_4H_6]Ph\}I$ as a green solid. ^1H NMR (C_6D_6):[30] 4.01 [d, $^3J_{P-H} = 2$ Hz, C_5H_5], 4.04 [d, $^3J_{P-H} = 2$ Hz, C_5H_5]. $^{31}P\{^1H\}$ NMR (C_6D_6): 74.0 (s), 78.0 (s). A mixture of $CpFe(CO)\{P[R,R\text{-}Me_2C_4H_6]Ph\}I$ (ca. 10 mg) and MeLi (ca.10 mg) in C_6D_6 (1 mL) was heated at 80 °C overnight. After this period, the volatile components were removed from the mixture in vacuo, and the residue was extracted into pentane (2 mL) and filtered. The pentane was removed from the filtrate to give $CpFe(CO)\{P[R,R\text{-}Me_2C_4H_6]Ph\}Me$ as a brown solid. IR Data (cyclohexane, cm^{-1}): 1913 (s). ^1H NMR (C_6D_6):[30] 0.09 [d, $^3J_{P-H} = 6$ Hz, $Fe-CH_3$], 0.41 [d, $^3J_{P-H} = 5$ Hz, $Fe-CH_3$], 4.06 [d, $^3J_{P-H} = 1$ Hz, C_5H_5], 4.11 [d, $^3J_{P-H} = 1$ Hz, C_5H_5]. $^{31}P\{^1H\}$ NMR (C_6D_6): 87.0 (s), 90.6 (s).

(b) Photolytic reaction of $CpFe(CO)_2Me$ (ca. 10 mg) with $PhP[R,R\text{-}Me_2C_4H_6]$. A mixture of $CpFe(CO)_2Me$ (ca. 10 mg) and $PhP[R,R\text{-}Me_2C_4H_6]$ (ca.10 mg) in C_6D_6 (1 mL) was photolyzed for 3 h. After this period, the volatile components were removed from the mixture in vacuo, and the residue was extracted into pentane (2 mL) and filtered, and pentane was removed from the filtrate to give $CpFe(CO)\{P[R,R\text{-}Me_2C_4H_6]Ph)\}Me$ as a brown solid.

(c) Thermal reaction of $CpFe(CO)_2Me$ with $PhP[R,R\text{-}Me_2C_4H_6]$. A mixture of $CpFe(CO)_2Me$ (ca. 10 mg) and $PhP[R,R\text{-}Me_2C_4H_6]$ (ca.10 mg) in C_6D_6 (1 mL) was heated at 80 °C for 5 days. After this period, the volatile components were removed from the mixture in vacuo, and the residue was extracted into pentane (2 mL) and filtered. The pentane was removed from the filtrate to give a mixture of $CpFe(CO)\{P[R,R\text{-}Me_2C_4H_6]Ph\}Me$ and $CpFe(CO)\{P[R,R\text{-}Me_2C_4H_6]Ph\}[C(O)Me]$ as a brown solid. Spectral data for $CpFe(CO)\{P[R,R\text{-}Me_2C_4H_6]Ph\}[C(O)Me]$: IR Data (cyclohexane, cm^{-1}): 1914 [$\nu(C{\equiv}O)$], 1609 [$\nu(C{=}O)$]. ^1H NMR (C_6D_6):[30] 2.67 [s, $Fe-C(O)CH_3$], 2.83 [d, $^4J_{P-H} = 1$ Hz, $Fe-C(O)CH_3$], 4.11 [d, $^3J_{P-H} = 1$ Hz, C_5H_5], 4.21 [d, $^3J_{P-H} = 1$ Hz, C_5H_5]. $^{31}P\{^1H\}$ NMR (C_6D_6): 83.7 (s), 83.9 (s).

X-ray Structure Determinations. X-ray diffraction data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector and crystal data, data collection and refinement parameters are summarized in Table 4. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 5.03).[30] Hydrogen atoms on carbon were included in calculated positions. The CO and Cl ligands of $Ir\{P[(C_5Me_4)_2]Ph\}_2(CO)Cl$ and *trans*-$Ir\{PPh[(R,R)\text{-}Me_2C_4H_6]\}_2(CO)Cl$ are disordered, which is a common feature of such complexes.[31] As a consequence, the bond lengths associated with these ligands are not necessarily accurate.[32]

Summary

In conclusion, the chiral monodentate phosphine $PhP[(C_5Me_4)_2]$ has been synthesized by oxidation of $Li_2[PhP(C_5Me_4)_2]$ with I_2. The steric and electronic properties of $PhP[(C_5Me_4)_2]$ are intermediate between those of PPh_2Me and PPh_3. Thus, structural characterization of several derivatives indicates that the crystallographic cone angles increase in the sequence: PPh_2Me (134.5°) < $PhP[(C_5Me_4)_2]$ (140.2°) < PPh_3 (148.2°). Likewise, the electron donating abilities of these phosphines, as judged by the ν(CO) stretching frequencies of $Ir(PR_3)_2(CO)Cl$ in Nujol, decrease in the sequence: PPh_2Me (1950 cm^{-1}) > $PhP[(C_5Me_4)_2]$ (1955 cm^{-1}) > PPh_3 (1961 cm^{-1}). Finally, $PhP[(C_5Me_4)_2]$ has a smaller cone angle and is less electron donating than the structurally similar phosphine, $PhP[Me_2C_4H_6]$.

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Supporting Information Available: X-ray crystallographic files in CIF format for all structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) A sub-stoichiometric amount of I_2 is used because $PhP[(C_5Me_4)_2]$ reacts with excess I_2.

(30) ^1H NMR data are not listed for the phosphine ligand due to its complexity.

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(33) The mean Ir−Cl, Ir−CO, and C−O bond lengths for complexes listed in the CSD (Version 5.20) are 2.41, 1.87, and 1.15 Å, respectively.

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