[12] The structures of racemic **4**, **13**, and **14** have been determined by X-ray crystallography. CCDC-184691 (**4**), CCDC-184693 (**13**), and CCDC-184694 (**14**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

[13] For examples of other metal-catalyzed asymmetric reactions that show strong solvent effects on enantioselectivity, see: a) Y. Sato, N. Saito, M. Mori, *J. Am. Chem. Soc.* **2000**, *122*, 2371; b) M. Ogasawara, H. Ikeda, T. Nagano, T. Hayashi, *J. Am. Chem. Soc.* **2001**, *123*, 2089.

[14] CCDC-184692 ((1*R*,2*S*)-**4**) contains the supplementary crystallographic data for this paper.[12] The single crystal used for the structure determination was obtained from an optically active sample of **4** with 82% *ee*. The small absolute structure parameter of 0.15(12) derived from the structure determination confirms the chirality of the crystal.

[15] Following the procedures reported by Dauban and Dodd for preparation of iminoiodane $PhI{=}NSO_2(CH_2)_2SiMe_3$ from $PhI(OAc)_2$ and $Me_3Si(CH_2)_2SO_2NH_2$ (P. Dauban, R. H. Dodd, *J. Org. Chem.* **1999**, *64*, 5304).

[16] ^1H NMR ($CDCl_3$, 400 MHz) of **19**: $\delta = 7.89$ (d, $J = 7.8$ Hz, 2H), 7.54 (t, $J = 7.4$ Hz, 1H), 7.33 (t, $J = 7.7$ Hz, 2H), 7.16 (m, 4H), 5.19 (m, 1H), 3.06 (m, 4H). The rather high instability of **19** renders it difficult to characterize this compound fully.

[17] The lower *ee* value in the catalytic reaction than in the reaction between **2** and **19** may arise from a lower loading of **2** in the former case. We once observed that reducing the loading of **2** from 10 to 2 mol% in the amidation of **6** in CH_2Cl_2, under otherwise the same conditions, led to a decrease in the *ee* value of **11** from 46 to 39%. Notice that some other metal-catalyzed asymmetric reactions also show significant dependence of enantioselectivity on catalyst loading (see for example: H. M. L. Davies, T. Hansen, M. R. Churchill, *J. Am. Chem. Soc.* **2000**, *122*, 3063).

A New Approach to Metalated Imido and Amido Tellurophosphoranes[**]

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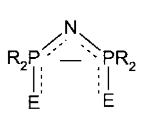
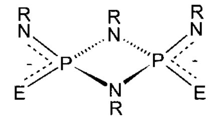
Masood Parvez

Monoanionic ligands of the type $[R_2P(E)NP(E)R_2]^-$ **1** have been investigated extensively as ligands for both main group elements[1] and transition metals.[2] This widespread interest stems from their potential uses as lanthanide shift reagents,[2] industrial catalysts,[3] luminescent materials,[4] or in metal extraction processes.[5] Recently we[6] and Stahl et al.[7] reported the first ambidentate dianionic ligands $[RN(E)P(\mu\text{-}NR)_2P(E)NR]^{2-}$ **2**, which adopt a variety of bonding modes, that is *N,E*, *N,N'*, or *E,E'*, with metal centers.

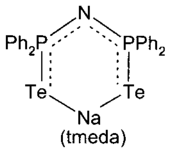


1 (E = O, S, Se)



2 (E = S, Se)

Despite this intense activity, the tellurium analogues of **1** and **2** are unknown. Anionic tellurophosphinic amides of the type $[tBu_2P(Te)NR]^-$ (R = *i*Pr, Cy) can be prepared by lithiation of $[tBu_2P(Te)NHR]$ with Li*n*Bu, and chelate complexes of this anion with Group 12 metals have been investigated as single-source precursors of binary metal tellurides.[8] Although ditellurides of the type $[R(Te)P(\mu\text{-}NtBu)_2P(Te)R]$ (R = Me, *t*Bu) have been reported,[9] our attempts to oxidize $tBuN(H)P(\mu\text{-}NtBu)_2PN(H)tBu$ with an excess of elemental tellurium in boiling toluene produced only the monotelluride $[tBuNH(Te)P(\mu\text{-}NtBu)_2PN(H)tBu]$ in about 5% yield.[10] Endeavors to generate $(TePPh_2)_2NH$ in a similar manner have also been unsuccessful. Consequently, we adopted a different approach to the synthesis of the anionic ligands **1** (E = Te) and **2** (E = Te), which involves metalation of the neutral imido or amido precursor prior to the reaction with tellurium.[11] Herein, we report the synthesis and X-ray structures of $[\{[Na(tmeda)][(TePPh_2)_2N]\}_2]$ (**3**) and $[Li(tmeda)]_2[Te(NtBu)P(\mu\text{-}NtBu)_2P(NtBu)Te]$ (**4**), (tmeda = tetramethylethylenediamine), which contain the first examples of **1** (E = Te) and **2** (E = Te), respectively.



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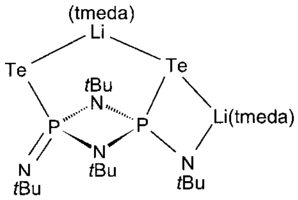

4

The reaction of $Na[Ph_2PNPPh_2]$ with tellurium powder in hot toluene in the presence of TMEDA produced **3** as moisture-sensitive, yellow crystals in 33% yield. The molecular structure of **3** (Figure 1) was determined by X-ray diffraction[12] on crystals obtained from hexane. The ditelluroimidodiphosphinate ligand **1** (R = Ph, E = Te) is *Te,Te'* chelated to sodium and forms a centrosymmetric dimer through Na–Te interactions. This is the first example of *Te,Te'* chelation to an alkali metal. The coordination sphere of the Na^+ ions is completed by one *N,N'* chelating tmeda ligand. A similar structure has been reported for the sodium salt of a monothioimidodiphosphinate $[\{Na(thf)_2[(OPPh_2)(SPPh_2)N]\}_2]$.[13] The central Na_2Te_2 ring in **3** is almost square-planar (bond angles at Na1 and Te1 are 87.51(5) and 92.49(5)°, respectively) with Na–Te distances of 3.143(2) and 3.181(2) Å, which are close to the value of 3.16 Å predicted from the ionic radii[14] and much shorter than the weak Na–Te interactions (3.494(3) Å) in the tellurolate $[Na(tmeda)_2][Te(2,4,6\text{-}Me_3C_6H_2)]$.[15] The P–Te bond lengths of 2.383(1) and 2.403(1) Å are only slightly longer than the values of about 2.37 Å determined for $tBu_3P{=}Te$[16] and amino-substituted tellurophosphoranes.[9c,17] The shorter P–

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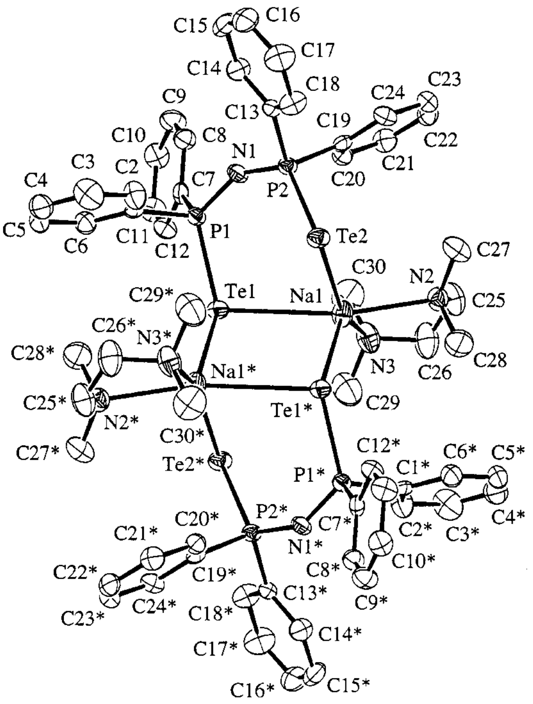

Figure 1. X-ray crystal structure of **3**. Selected bond lengths [Å] and angles [°]: P1-N1 1.591(4), P2-N1 1.589(4), P1-Te1 2.4029(13), P2-Te2 2.3827(13), Na1-Te1 3.143(2), Na1-Te2 3.259(2), Na1-Te1* 3.181(2); P1-N1-P2 143.3(3), N1-P1-Te1 122.18(15), N1-P2-Te2 120.88(15), P1-Te1-Na1 104.20(5), P2-Te2-Na1 93.10(5), Te1-Na1-Te2 84.69(5), Te1-Na1-Te1* 87.51(5), Na1-Te1-Na1* 92.49 (5). Symmetry transformations used to generate equivalent atoms: * $-x$, $-y$, $-z+2$.

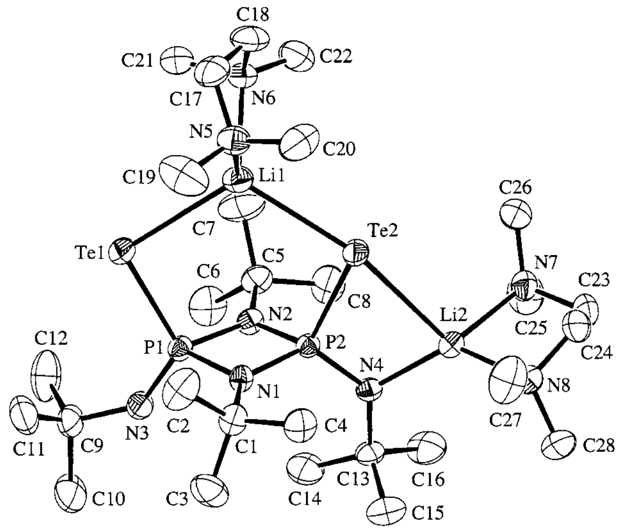

Figure 2. X-ray crystal structure of **4**. Selected bond lengths [Å] and angles [°]: Li1-Te1 2.842(5), Li1-Te2 2.791(5), Li2-Te2 2.865(5), Li2-N4 1.973(5), P1-Te1 2.4515(8), P2-Te2 2.4243(7), P1-N3 1.534(2), P2-N4 1.574(2); Te1-Li1-Te2 113.35(17), N4-Li2-Te2 80.93 (18), N3-P1-Te1 119.94(11), N4-P2-Te2 104.89(9), P2-Te2-Li2 65.59 (10), P2-Te2-Li1 96.51(10), Li1-Te2-Li2 160.06(14), P1-Te1-Li1 97.15(11).

Te bond is associated with the two-coordinate tellurium center, which also participates in the longer Te–Na bond (3.259(2) Å) in the six-membered NP_2Te_2Na ring. The ^{31}P NMR and ^{125}Te NMR spectrum of **3** in $[D_8]$THF at 235 K reveal single environments for both the phosphorus and tellurium atoms. This observation may be attributed to a fast exchange process involving the Na and Te sites or to dissociation into a monomer in which the Na^+ ion is solvated by THF. The coupling constant $^1J_{(P,Te)} = 1619$ Hz is, as expected, significantly smaller than the values of 1663–2095 Hz reported for neutral tellurophosphoranes.[18]

The treatment of $[Li(thf)]_2[t\mathrm{Bu}NP(\mu\text{-}Nt\mathrm{Bu})_2PNt\mathrm{Bu}]$ with tellurium powder in toluene at 80 °C in the presence of TMEDA produces **4** as yellow, moisture-sensitive crystals in 19 % yield. The molecular structure of **4** (Figure 2) was determined on single crystals obtained from hexane.[19] The structure reveals a unique bonding mode for ligands of the type **2** in which one Li^+ ion is coordinated in a *Te,Te′* fashion, while the second Li^+ ion is *N,Te* chelated by the dianion. By contrast, the sulfur analogue, **4** (E = S), exhibits bis-*N,S* chelation to two Li^+ centers.[6b] The X-ray structures of $Li[t\mathrm{Bu}_2P(Te)NR]$ ($R = i$Pr, Cy) were not determined, but chelate complexes of the anion with transition metals are *N,Te* bonded.[8] The P–Te bond length involving the two-coordinate Te center in **4** is 0.027 Å longer than that involving the three-coordinate Te atom, presumably because the former is associated with the shorter exocyclic P–N bond (1.534(2) versus 1.574(2) Å). The mean value of d(P–Te) in **4** is, as expected, significantly longer by about 0.07 Å than the value of 2.370(1) Å found for the monotelluride $[t\mathrm{Bu}NH(Te)P(\mu\text{-}Nt\mathrm{Bu})_2PN(H)t\mathrm{Bu}]$.[10] The NMR data for **4** in $[D_8]$toluene demonstrate that the novel, asymmetric coordination of the two Li^+ ions to the dianion **2** observed in the solid state is maintained in solution at 235 K. Thus, the ^{7}Li NMR spectrum of **4** in $[D_8]$toluene exhibits two well-separated resonance signals at $\delta = 0.70$ and 3.88 ppm, while the ^{31}P NMR spectrum shows two singlets (with ^{125}Te satellites) at $\delta = -113.7$ and -75.3 ppm. Consistently, the ^{125}Te NMR spectrum displays two doublets at $\delta = -289$ and -87 ppm. The smaller values of $^1J_{(P,Te)}$, 1309 and 1467 Hz, are consistent with the longer P–Te bond lengths in **4** compared to those in **3**.

In summary, the discovery of a new approach to the previously inaccessible ditelluroimidodiphosphinate anion **1** (E = Te) and the ditellurodiimidocyclodiphosph(V/V)azane dianion **2** (E = Te) paves the way for extensive investigations of the coordination chemistry of these tellurium-centered ligands. Semiempirical PM3 calculations indicate that the success of this method can be attributed to an increase in the nucleophilicity of the phosphorus(III) centers in $(PPh_2)_2NH$ and $t\mathrm{Bu}N(H)P(\mu\text{-}Nt\mathrm{Bu})_2PN(H)t\mathrm{Bu}$ upon metalation. Details of this study, as well as additional examples of the successful application of this approach to the synthesis of novel NP(V)Te anions, will be discussed in a full account of this work.

Experimental Section

All manipulations were carried out under anaerobic and anhydrous conditions. NMR spectra were obtained on $[D_8]$THF (**3**) or $[D_8]$toluene (**4**) solutions at 235 K using a Bruker DRX 400 MHz spectrometer.

3$\cdot 0.25\,C_6H_{14}$: A mixture of $Na[Ph_2PNPPh_2]$[20] (0.100 g, 0.245 mmol), tellurium powder (0.063 g, 0.49 mmol), and TMEDA (0.114 g, 0.982 mmol) in toluene (5 mL) was heated to 80 °C for 3 h. After cooling to 23 °C, the mixture was centrifuged and decanted to remove unreacted tellurium. Yellow crystals of **3**$\cdot(C_6H_{14})_{0.25}$ (0.065 g, 33 %) were obtained after one day at 23 °C. Elemental analysis calcd for $C_{31.5}H_{39.5}N_3NaP_2Te_2$: C 47.27, H 4.97, N

5.25; found: C 48.42, H 5.35, N 5.32; $^{31}P\{^1H\}$ NMR: $\delta = 9.5$ ppm (s, $^1J_{(P,Te)} = 1632$ Hz); ^{125}Te NMR: $\delta = -403.6$ ppm (d, $^1J_{(P,Te)} = 1619$ Hz).

4: A mixture of $[Li(thf)]_2[tBuNP(\mu\text{-}NtBu)_2NtBu]$[21] (0.200 g, 0.396 mmol), tellurium powder (0.101 g, 0.79 mmol), and TMEDA (0.368 g, 3.17 mmol) in toluene (5 mL) was heated at 80 °C for 3 h. The mixture was centrifuged and the supernatant was decanted from unreacted tellurium. After removal of solvent under vacuum, the product was redissolved in *n*-hexane (ca. 1 mL). Yellow crystals of **4** (0.062 g, 19 %) were deposited after one day at 23 °C. Elemental analysis calcd for $C_{28}H_{68}Li_2N_8P_2Te_2$: C 39.66, H 8.08, N 13.22; found: C 38.06, H 8.23, N 12.25; ^1H NMR ([D$_8$]toluene, 235 K): $\delta = 1.62$ (s, 9 H; N*t*Bu), 1.97 (s, 9 H; N*t*Bu), 2.18 (s, 18 H; μ-N*t*Bu), 2.20 (s, 12 H; NMe$_2$), 2.30 ppm (s(br), 8 H; NCH$_2$); $^{31}P\{^1H\}$ NMR: $\delta = -113.7$ (s, $^1J_{P,Te} = 1467$ Hz), -75.3 ppm (s, $^1J_{P,Te} = 1309$ Hz); ^7Li NMR: $\delta = 0.70$ (s), 3.88 ppm (s); ^{125}Te NMR: $\delta = -289$ (d, $^1J_{Te,P} = 1352$ Hz), -87 ppm (d, $^1J_{Te,P} = 1486$ Hz). The values of $^1J_{Te,P}$ obtained from the ^{31}P NMR spectrum are more reliable than those obtained from the ^{125}Te NMR spectrum owing to the broad line widths ($\Delta\upsilon_{1/2} \sim 225$ Hz) in the latter spectrum.

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[1] For recent reviews, see: a) S. Silvestru, J. E. Drake, *Coord. Chem. Rev.* **2001**, *223* 117–216; b) J. D. Woollins, *J. Chem. Soc. Dalton Trans.* **1996**, 2893–2901.

[2] H. Rudler, B. Denise, J. R. Gregorio, J. Vaissermann, *Chem. Commun.* **1997**, 2299–2300.

[3] W.-H. Leung, H. Zheng, J. L. C. Chim, J. Chan, W.-T. Wong, I. D. Williams, *J. Chem. Soc. Dalton Trans.* **2000**, 423–430.

[4] S. W. Magennis, S. Parsons, A. Corval, J. D. Woollins, Z. Pikramenou, *Chem. Commun.* **1999**, 61–62.

[5] J. G. H. du Preez, K. U. Knabl, L. Krüger, B. J. A. M. van Brecht, *Solvent Extr. Ion Exch.* **1992**, *10*, 729.

[6] a) T. Chivers, M. Krahn, M. Parvez, *Chem. Commun.* **2000**, 463–464; b) T. Chivers, M. Krahn, M. Parvez, G. Schatte, *Inorg. Chem.* **2001**, *40*, 2547–2553; c) T. Chivers, C. Fedorchuk, M. Krahn, M. Parvez, G. Schatte, *Inorg. Chem.* **2001**, *40*, 1936–1942.

[7] G. R. Lief, C. J. Carrow, L. Stahl, *Organometallics* **2001**, *20*, 1629–1635.

[8] a) M. Bochmann, G. C. Bwembya, N. Whilton, X. Song, M. B. Hursthouse, S. J. Coles, A. Karanlov, *J. Chem. Soc. Dalton Trans.* **1995**, 1887–1892; b) M. Bochmann, G. C. Bwembya, M. B. Hursthouse, S. J. Coles, *J. Chem. Soc. Dalton Trans.* **1995**, 2813–2817.

[9] a) O. J. Scherer, G. Schnabl, *Chem. Ber.* **1976**, *109*, 2996–3004; b) O. J. Scherer, G. Schnabl, *Angew. Chem.* **1977**, *89*, 500–501; *Angew. Chem. Int. Ed. Engl.* **1977**, *16*, 486; c) S. Pohl, *Z. Naturforsch. Sect. B* **1978**, *33*, 610–613; S. Pohl, *Z. Naturforsch. B* **1979**, *34*, 256–261.

[10] G. Briand, T. Chivers, M. Krahn, *Coord. Chem. Rev.* **2002**, in press.

[11] G. Briand, T. Chivers, G. Schatte, M. Parvez, Abstract No. 475, 84th CSC Conference and Exhibition (Montreal), **2001**.

[12] Crystal data for $\mathbf{3}\cdot 0.25\,C_6H_{14}$: $C_{30}H_{36}N_3NaP_2Te_2\cdot 0.25\,C_6H_{14}$, $M_r = 800.29$, tetragonal, space group $I4_1/a$, $a = 35.7317(12)$, $c = 11.0884(3)$ Å, $V = 14{,}157.2(8)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.502$ g cm^{-3}, $F(000) = 6312$, $T = 173(2)$ K. Data were collected on a Nonius Kappa CCD diffractometer on a yellow needlelike crystal ($0.25 \times 0.08 \times 0.04$ mm^3) coated with Paratone 8277 oil and mounted on a glass fiber using ω and ϕ scans. Of the 11182 reflections collected, 6186 were unique ($R_{int} = 0.040$) and 4424 were observed [$I \geq 2.00\sigma(I)$] and used to refine 355 parameters. The structure was solved by direct methods (SIR92) expanded with Fourier techniques (DIRDIF94), and refined by SHELXL97. The non-hydrogen atoms were refined anisotropically. A disordered molecule of *n*-hexane was also located in the lattice with three carbon atoms (site occupancy 0.5 each) disordered over a wide area with large displacement parameters; these atoms were included with isotropic parameters. Hydrogen atoms were included at geometrically idealized positions and not refined; hydrogen atoms of the hexane solvate were ignored. Refinement by least-squares calculations converged at $R_1 = 0.038$ and $wR_2 = 0.083$.

[13] J. Yang, J. E. Drake, S. Hermandez-Ortega, R. Rösler, C. Silvestru, *Polyhedron* **1997**, *16*, 4061–4071.

[14] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, **1960**, p. 514.

[15] P. J. Bonasia, J. Arnold, *J. Chem. Soc. Chem. Commun.* **1990**, 1299–1301.

[16] N. Kuhn, H. Schumann, G. Wolmershäuser, *Z. Naturforsch. B* **1987**, *42*, 674–678.

[17] C. Rømming, A. J. Iversen, J. Songstad, *Acta Chem. Scand. Ser. A* **1980**, *34*, 333–342.

[18] a) C. H. W. Jones, R. D. Sharma, *Organometallics* **1987**, *6*, 1419–1423; b) N. Kuhn, G. Henkel, H. Schumann, R. Fröhlick, *Z. Naturforsch. B* **1990**, *45*, 1010–1018.

[19] Crystal data for **4**: $C_{28}H_{68}Li_2N_8P_2Te_2$, $M_r = 847.92$, monoclinic, space group $P2_1/c$, $a = 17.8810(3)$, $b = 9.7701(2)$, $c = 24.0003(5)$ Å, $\beta = 91.6451(6)°$, $V = 4191.10(14)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.344$ g cm^{-3}, $F(000) = 1728$, $T = 170(2)$ K. Data were collected on a Nonius Kappa CCD diffractometer on a yellow plate ($0.20 \times 0.15 \times 0.08$ mm^3) coated with Paratone 8277 oil and mounted on a glass fiber using ω and ϕ scans. Of the 16883 reflections collected 9529 were unique ($R_{int} = 0.028$) and 7266 were observed [$I > 2.00\sigma(I)$] and used to refine 379 parameters. Structure solution and refinement followed the procedures described above for **3**. Refinement by least-squares calculations converged at $R_1 = 0.034$ and $wR_2 = 0.072$. CCDC-184064 and CCDC-184065 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[20] Prepared by a modification of the procedure reported by: J. Ellermann, M. Schütz, F. W. Heinemann, M. Moll, *Z. Anorg. Allg. Chem.* **1998**, *624*, 257–262.

[21] I. Schranz, L. Stahl, R. J. Staples, *Inorg. Chem.* **1998**, *37*, 1493–1498.

Metallabenzenes and Valence Isomers. Synthesis and Characterization of a Platinabenzene**

Volker Jacob, Timothy J. R. Weakley, and Michael M. Haley*

Dedicated to Professor Gottfried Huttner on the occasion of his 65th birthday

In our group we have developed a convenient method for the preparation of iridabenzenes starting from the C_5 synthetic equivalent *Z*-3-(2-iodovinyl)-1,2-diphenylcyclopropene (**1**).[1] Using this precursor, iridabenzene synthesis can also be carried out in a stepwise manner via an iridabenzvalene intermediate, which could be characterized and converted into the corresponding iridabenzene by thermal treatment.[2] In addition to varying the coordination pattern at the iridium center and the substituents on the vinylcyclopropene precursor,[3] we are currently trying to show this concept to be generally applicable for the synthesis of metallabenzenes and

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