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Tertiary Phosphines, P-Chiral Phosphinites and Phosphonic Acid Esters Bearing Fullerene Substituent. Metal Complexes and Redox Properties

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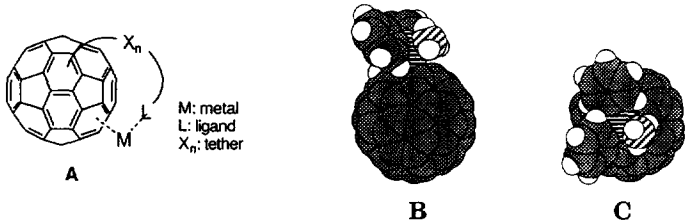
Abstract: The reaction of a lithiated phosphine-borane or a phosphinite borane with C_{60} followed by removal of the BH_3 group affords a phosphine or a phosphinite bearing a fullerene substituent. Alternatively, the addition of $(MeO)_2POLi$ to C_{60} affords a fullerene-substituted phosphonic acid ester. The phosphine compounds complex with BH_3 and $PtCl_2$ selectively on the phosphorus atom with 1:1 and 2:1 stoichiometry, respectively, and these compounds show multi redox properties as revealed by electrochemical measurements.

Design and synthesis of organometallics bearing multi redox-active ligands are important subject of chemical research, since they will serve as new catalysts for organic reactions or as new molecular device in material science. Since fullerenes have been shown to possess multi-redox properties, and found to act as good ligands for transition metals as well, metal complexes of fullerenes belong to a particularly intriguing class of compounds. Electrochemical studies of low valent Group 10 metal-C_{60} complexes revealed, however, that complexes of metal with C_{60} itself are unstable under reduced conditions, presumably due to dissociation of the reduced C_{60} ligand from the metal.[1]

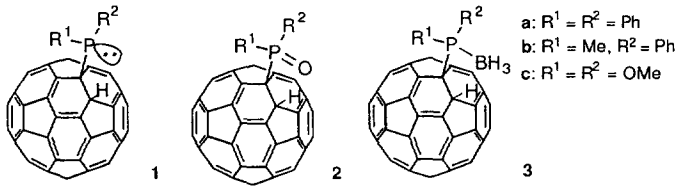
We report here a new approach for the synthesis of a multi-redox organometallic complexes of fullerenes as represented by the general structure **A**, where an internal ligand L would capture the central metal atom regardless of the oxidation state of the fullerene group. In view of the versatility of organophophorus ligands in metal complexation, we selected a phosphorus group as the L group. For the sake of simplicity, the number of the connecting tether n was selected to be zero in this initial study.[2] These metal complexes are interesting not only as a multi-redox catalyst, but also as a bidentate ligand bearing "push"(phosphorus) and "pull" (C_{60}) groups. This class of tertiary phosphines ("bucky phosphines" **1**), including P-

chiral derivatives **8** and **11** would serve as a prototype for design of new metal ligands for asymmetric synthesis.

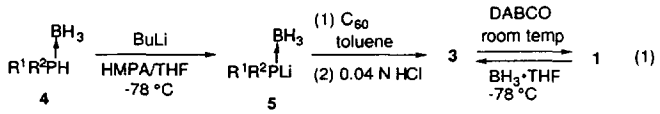


Results and Discussion

Synthesis of Bucky Phosphines. Taking advantage of the electrophilic nature of C_{60},[3] we focused on the nucleophilic reactivity of a metalated phosphine-borane **5**. The borane complex of a secondary phosphine **4** is air-stable, easy to handle, and available in a single step by reduction of R^1R^2PCl with a mixture of BH_3 and $LiAlH_4$ in THF.[4] The proton attached to the phosphorus atom in **4** can be easily deprotonated to give the corresponding anion **5**.[5] Therefore, the synthesis of bucky phosphine was achieved in a straightforward manner by the addition of a metalated phosphine-borane to C_{60} followed by removal of the borane group from the adduct with diazabicyclo[2.2.2]octane (DABCO). The $C_{60}H$ group in **1** is an unusual sp3 alkyl substituent with steric bulk, photoactivity[6] and potential to bind to certain metal atoms.[7] The bucky phosphines have considerable thermal stability, and, notably, the P-chiral phosphinite **8** was also found to be configurationally stable. As is seen in the MNDO optimized structure (**B** and **C**, borane atom marked by hatching) of the borane complex **3a**,[8] the $C_{60}H$ group brings about considerable steric congestion and creates a novel coordination sphere in the metal complex.

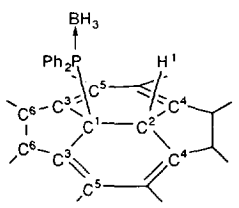


We initially attempted the addition of diphenylphosphine itself to C_{60}, as the addition of an isoelectronic secondary amine to C_{60} is a facile process.[9] However, the phosphine was inert to C_{60} even at an elevated temperature. Therefore, we looked into a more nucleophilic reagent. While lithiated diphenylphosphine generated by BuLi deprotonation of diphenylphosphine reacted with C_{60} (about 30% yield based on HPLC analysis), separation of the adduct from unreacted C_{60} and other side products of much the same polarity on silica gel was practically impossible.



We envisaged that a polar phosphorus-borane bond in phosphine-borane complex will not only stabilize the phosphorus atom against oxidation but facilitate product separation. We found that **5** readily adds across the strained and electron-deficient double bond of buckminsterfullerene,[10] and the product was easily separated from the reaction mixture. Thus, addition of $Ph_2PLi•BH_3$ prepared by BuLi-deprotonation of $Ph_2PH•BH_3$ (2 equiv) in THF to toluene solution of C_{60} took place at -78 °C (1 h) to give the adduct **3a** in 82% isolated yield after quenching with HCl in ethyl acetate. The adduct **3a** was more polar (R_f 0.21, 20% toluene in hexane) than C_{60} (R_f 0.71) and could be readily purified by silica gel chromatography. The reaction of $MePhPLi•BH_3$ also took place smoothly, albeit slowly, at -40°C to give the adduct **1b** in 46% yield. The optically active reagent (+)-$PhMePLi•BH_3$ underwent racemization at this temperature, while at lower temperature the reaction was too slow. The borane complexes thus obtained were found to be stable in air at room temperature for months.[11]

Scheme I



3a

H^1 = δ 6.9 [$^3J(PH^1)$= 25.7 Hz]
C^1 = δ 65.5 [$^1J(PC^1)$ = 32.4 Hz]
C^2= δ 58.2 [$^2J(PC^2)$ = 9.5 Hz]
C^3 or C^4 = δ 149.76 [J(PC) = 4.8 Hz] or
δ 152.54 [J(PC) = 5.7 Hz]
C^5 or C^6 = δ 135.79 [^3J(PC) = 2.0 Hz] or
δ 137.25 [^3J(PC) = 4.8 Hz)]
P = δ 39.98 [^1J(PB) = 44.2 Hz)]
B = δ -58.74

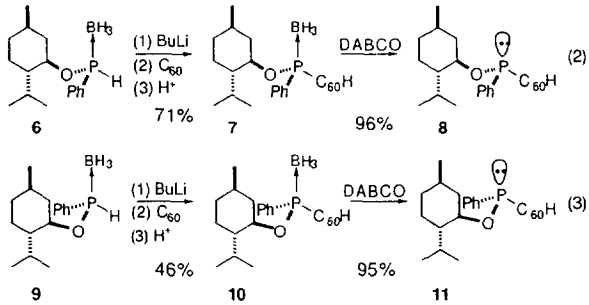
The structure of the phosphine-borane **3a** was assigned by ^1H, ^{13}C, ^{11}B and ^{31}P NMR spectroscopy, which indicated that the addition reaction to C_{60} took place exclusively at the 6,6-ring junction. In the ^1H NMR spectrum of **3a**, the H^1 atom (Scheme I) appears as a doublet at δ 6.94 ppm. (J_{P-H} = 25.7 Hz). The large P-H coupling is consistent with the vicinal and *cis* relative stereochemistry between H^1 and the phosphorus atom.[12]

The $^{13}C\{^1H, ^{31}P\}$ NMR spectrum of **3a** ($CDCl_3/CS_2$; $CDCl_3$ as δ 77.0 ppm) showed 30 sp2 signals and two sp3 signals in the C_{60} region, indicating the Cs symmetry of the molecule. Partial assignment of the signals due to C^1 to C^6 in Scheme I was made on the basis of the magnitude of P–C coupling and the chemical shift values. The doublet at δ 66.5 ppm in $^{13}C\{^1H\}$NMR is coupled strongly (32.4 Hz) to the phosphorus atom and hence assigned to C^1. Another sp3 carbon at δ 58.2 ppm with small coupling (J_{P-C} = 9.5 Hz) was assigned to C^2. The C^3–C^6 atoms exhibit long range coupling with the phosphorus atom. The $^{11}B\{^1H\}$ NMR

($CDCl_3/CS_2$; H_3BO_3 as δ 0.3 ppm) showed a single broad signal at δ -58.74 ppm, and the $^{31}P\{^1H\}$ NMR ($CDCl_3/CS_2$; 85% H_2PO_4 as δ 0.0 ppm) also showed a single signal appearing at δ 39.98 ($J_{B\text{-}P}$ = ca. 44.2 Hz). The relatively small value of the $J_{B\text{-}P}$ coupling constant (cf. $Ph_3P{\bullet}BH_3$; $J_{11B\text{-}P}$ = 57 Hz)[13] suggests[14] that the $C_{60}H$ group is a stronger electron withdrawing group than a phenyl group. The reaction of **1a** with 1 equiv of $BH_3{\bullet}THF$ at -78 °C selectively took place on the phosphorus atom to give back **3a** in quantitative yield.[15]

Treatment of the borane complex **3a** with DABCO[16,17] (20 equiv) at room temperature for 1.5 h under nitrogen removed the borane group to give quantitatively the phosphine **1a** as black powder. The removal of the borane group caused systematic upfield shift of the ^1H NMR signals owing to the decreased electron withdrawal by the phosphorus atom. Thus, the proton on C_{60} was shifted upfield to δ 6.82 (J_{PH} = 15.6 Hz), and the phenyl ortho protons to δ 8.23 and 8.25. Treatment of **1a** with one equivalent of mCPBA gave the phosphine oxide **2a**.[18,19]

Starting from P-chiral phosphinite-borane, we could synthesize P-chiral compounds.[20] Thus, the (+)-menthyl phosphinite-borane[5b] **6** (2 equiv) was lithiated and added to C_{60} in a manner described above. The adduct **7** was isolated in 71% isolated yield (C_{C60}-*H*, δ 7.17, $J_{P\text{-}H}$ = 26.0 Hz) (eq 2). Alternatively, the lithium salt of the diastereomeric phosphinite-borane **9** gave **10** in 46% yield (C_{C60}-*H*, δ 7.00, $J_{P\text{-}H}$ = 26.0 Hz) (eq 3). The two adducts were diastereomerically pure by ^1H NMR, indicating that the addition took place stereospecifically (most likely with retention of the P-chirality as indicated in the scheme).[5,21] The B-P bond in a phosphinite-borane complex is so strong that it is generally difficult to remove the BH_3 group by amine treatment. However, the free phosphines **8** (C_{C60}-*H*, δ 6.86, $J_{P\text{-}H}$ = 13.7 Hz) and **11** (C_{C60}-*H*, δ 6.81, $J_{P\text{-}H}$ = 14.2 Hz) could be obtained in ca. 90% yield by treatment with 100-120 equiv of DABCO at room temperature for 15 h with complete retention of the phosphorus chirality. The P-chirality of the phosphinite **8** was found to be remarkably stable (no sign of epimerization upon heating for 14 h at 80 °C in degassed toluene).[22]



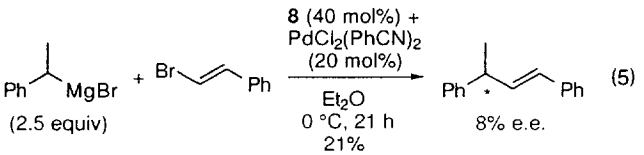
As an alternative synthetic approach to phosphorus-substituted C_{60}, we found that addition of a phosphite anion to C_{60} gives satisfactory results. Thus, the addition of the lithium salt **13**, which was generated by deprotonation of dimethyl phosphite (**12**) with BuLi, took place nicely to afford **2c** in 32% yield (51% based on consumed C_{60}). (eq 4).[23]

$$(MeO)_2POH \xrightarrow[HMPA/THF,\ -78\ ^\circ C]{BuLi} (MeO)_2POLi \xrightarrow[(2)\ 0.04\ N\ HCl]{(1)\ C_{60},\ toluene} \mathbf{2c} \qquad (4)$$

12 **13**

Synthesis and Reaction of Bucky Phosphine-Transition Metal Complexes. The phosphinite **8** formed a complex with $PtCl_2$. Treatment of **8** with $PtCl_2(PhCN)_2$ (0.5 equiv) in toluene afforded a clear solution, which yielded an analytically pure complex, $PtCl_2 \bullet \mathbf{8}_2$, as brown powder after concentration and precipitation from $CHCl_3$ with hexane. The ^{31}P NMR spectrum of the complex showed a single phosphorus signal appearing at δ 90.7 ppm with $J_{P\text{-}Pt}$ = 4.90 kHz, indicating that the metal is coordinated selectively to the phosphorus atom.

A palladium complex of **8**, prepared by treatment of **8** with 0.5 equiv of $PdCl_2(PhCN)_2$, catalyzed, albeit in low optical yield (8% e.e.), asymmetric cross coupling of 1-phenyl-1-ethylmagnesium bromide and β-bromostyrene to afford 1,3-diphenyl-1-butene (eq 5).[24] The observed chirality induction suggests that **8** remains coordinated to the palladium metal during catalytic turnover.



(5)

Redox Properties of Bucky Phosphine Derivatives. Cyclic voltammetry (CV) of the bucky phosphines and their borane complexes showed reduction profile similar to those of C_{60} and other organofullerenes (Table 1). CV of **1a** showed three single electron reduction events (-1.19, -1.54, and -2.05 V vs. ferrocene/ferrocenium in 1,2-dichlorobenzene, Figure 1). The first reduction potential of **1a** is ca. 0.04 V higher than that of the structurally related alkyl-substituted C_{60} derivatives, suggesting that the Ph_2P group is a weaker electron donor to C_{60} than an alkyl group, and is among the least electron-donating substituent on C_{60} so far reported.[25] As might be expected, the phosphine-borane **3a** was found to be easier to reduce (-1.17, -1.53, and -2.02 V) than the parent phosphine **1a**. The phosphinite borane **7** also showed close reduction events, and each of the reduction potentials is shifted 0.07-0.17 V to more negative potential relative to C_{60}. These similarity clearly indicated that only the fullerene moiety was reduced during these experiments. In all experiments, we observed a small new peak upon reversing the scan probably due to the formation of free C_{60}. Careful examination by changing the scan range revealed that the partial decomposition took place after the first reduction occurred.

Table 1. Half-Wave Potential by Cyclic Voltammetry[a]

compound	*E*1	*E*2	*E*3	*E*4	*E*5
C_{60}[b]	-1.13	-1.50	-1.95	-	-
1a	-1.19	-1.54	-2.05	-	-
2c	-1.16	-1.59	-1.93	-	-
3a	-1.17	-1.53	-2.02	-	-
7[c]	-1.21	-1.68	-2.12	-2.57	-
$PtCl_2$•$\mathbf{8}_2$[c]	-1.19	-1.61	-1.91	-2.17	-2.38

[a] V vs. ferrocene/ferrocenium couple; *n*-Bu_4NPF_6 (0.1 M) in 1,2-dichlorobenzene; scan rate = 20 mV/s; scan range = 0 - 2.27 V. [b]Taken from ref. 25. [c]Value obtained by differential pulse voltammetry: pulse amplitude, 50 mV; pulse width, 50 ms; pulse period, 200 ms; scan rate, 20 mV/s, scan range = 0 to -2.67 V. *E*3 and *E*5 waves are due to reduction of Pt from Pt(II) to Pt(I) and from Pt(I) to Pt(0), respectively; see text.

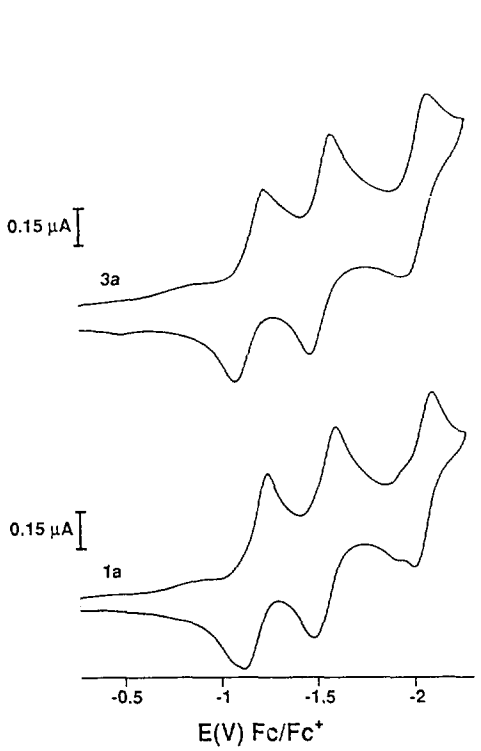


Figure 1. CV of **1a** and **3a**.

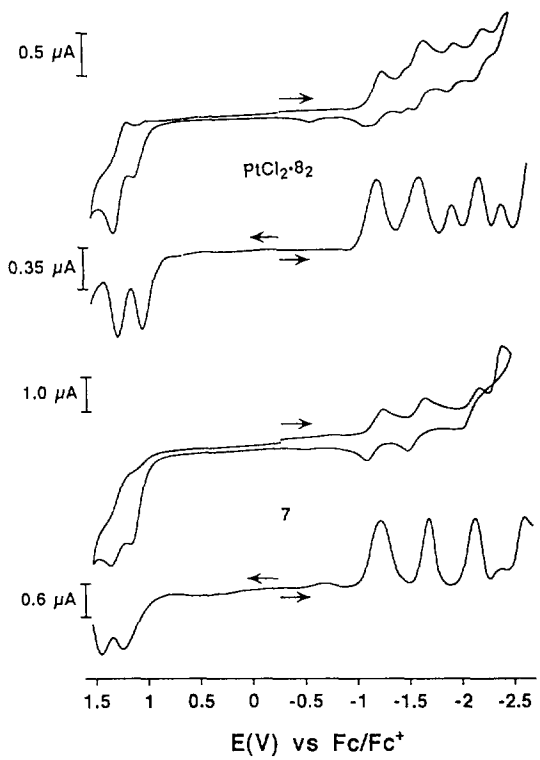


Figure 2. DPV of **7** and $PtCl_2$•$\mathbf{8}_2$.

Next, we examined how the reduction profile of the bucky phosphine is affected by the oxidation state of the center atom. Differential pulse voltammograms (DPV) of the complex in 1,2-dichlorobenzene showed five reduction potentials (-1.19, -1.61, -1.91, -2.17, -2.38 V) the first, second and fourth waves due to the C_{60} moiety and the third and fifth due to the platinum atom (Figure 2). Those assigned to the C_{60} reduction (0.48, 0.46, 0.41 μA, respectively) are twice as strong as the latter (0.20 and 0.19 μA, respectively), which is consistent with the 2:1 stoichiometry of the ligand/metal ratio. An independent single electron reduction of two phosphinite groups of $PtCl_2$•**8**$_2$ ($E1$, $E2$, and $E4$) indicated that mutual interaction between two phosphinite groups is unlikely. However, we found an electronic interaction between the metal and the phosphinite by comparison of the reduction potential of $PtCl_2$•**8**$_2$ and **7**. The first and the second reduction events of $PtCl_2$•**8**$_2$ (-1.19 and -1.61 V) took place at a lower value than that of **7** (-1.21 and -1.68 V), suggesting that Pt(II) is stronger Lewis acid than BH_3. However, after the single electron reduction of Pt(II) to Pt(I) ($E3$ of $PtCl_2$•**8**$_2$, -1.91 V), the third reduction of the C_{60} moiety in $PtCl_2$•**8**$_2$ ($E4$, -2.17 V) became harder than that of BH_3 complex ($E3$ of **7**, -2.12 V). The fourth reduction of C_{60} is more difficult for $PtCl_2$•**8**$_2$ than for **7** (at -2.57 V for **7**, Table 1, and at <2.7 V for $PtCl_2$•**8**$_2$, Figure 2 top), where the metal atom has already been reduced to the least Lewis acidic Pt(0) state. These results clearly showed that the redox profile of the ligand is significantly affected by the oxidation state of the center atom. Alternatively, the electronic state of the metal is expected to be altered by the redox state of the fullerene ligand.

We also found that the phosphonic acid ester **2c** shows three reduction events similar to that of other compounds. While the first and second events took place slightly lower than that of C_{60}, third reduction of **2c** was found to occur (albeit only slightly) on a more positive side than that of C_{60} (-1.93 V vs. -1.95 V, Table 1).

In summary, we have synthesized the first and the simplest member of C_{60}-containing metal ligands as represented by the general structure in **A** and shown that a transition metal complex possesses multi-redox property. The compounds reported above represent a new class of phosphorus compounds and suitable structural modification[26] would make them useful also for bioorganic investigation on buckminsterfullerenes.[27,28]

Experimental Section

^{1}H NMR (270, 400, and 500 MHz), ^{13}C NMR (100 and 125 MHz), ^{31}P NMR (203 and 162 MHz), ^{11}B NMR (128 MHz) spectra were measured for a $CDCl_3$ or $CS_2/CDCl_3$ (= 1/1) solution of a sample on JEOL GSX-270, EX-400, Alpha 400, and GSX-500 instruments. ^{1}H NMR spectra are reported in parts per million from internal tetramethylsilane, ^{13}C NMR spectra from $CDCl_3$ (77.0 ppm), ^{31}P NMR from external $P(OMe)_3$ (140.0 ppm) or external 85% H_3PO_4 (0.0 ppm), ^{11}B NMR from external H_3BO_3 (0.3 ppm). IR spectra are reported in cm^{-1}. Recycling preparative HPLC was performed on Japan Analytical Industry LC-908 machine equipped with GPC column (JAIGEL 1H and 2H) using $CHCl_3$ as eluent. Cyclic voltammetry and Differential pulse voltammetry were recorded on a BAS-B/W electrochemical analyzer as previously reported.[1] UV-vis spectra was recorded on HITACHI 330. CD spectra was recorded on JASCO J-500C. FAB mass spectra were recorded on a JEOL AX505 spectrometer.

Diphenyl(C_{60}H)phosphine-Borane 3a.

To a solution of diphenylphosphine-borane (488 mg, 2.44 mmol) and HMPA (0.77 mL, 4.44 mmol) in 5 mL of THF was added *n*-BuLi (1.52 mL of 1.46 M in hexane) at -78 °C under nitrogen, and the resulting solution was stirred for 2 h. This solution was added to a solution of C_{60} (800 mg, 1.11 mmol) in toluene (650 mL) through a cannula at -78 °C. After stirring for 1 h at this temperature, the reaction mixture was slowly warmed to room temperature over 1 h, and quenched by addition of 0.04 N HCl in ethyl acetate (ca. 50 mL). The reaction mixture was passed through a pad of silica gel (silica gel 50 g, elution with toluene). Removal of the solvent followed by purification by silica gel chromatography (silica gel 300 g, elution with hexane followed by 20% toluene in hexane) afforded **3a** (836.4 mg, 82 %) as brown powder. An analytically pure sample was obtained by purification on a recycling preparative HPLC. *Eox* = +1.07, *Ered1* = -1.17, *Ered2* = -1.53, *Ered3* = -2.02 V (vs. Fc/Fc^+); IR ($CHCl_3$) 3020, 2400, 1440, 1225, 1210, 790, 530; ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) 1.50-2.30 (br m, 3 H, BH_3), 6.94 (d, $^3J_{PH}$ = 25.7 Hz, 1 H, C_{60}H), 7.61-7.68 (m, 6 H, *m*- and *p*-C_6H_5), 8.51 (ddd, *J* = 14.2, 8.2, 1.7 Hz, 4 H, *o*-C_6H_5); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) 58.21 (d, $^2J_{CP}$ = 9.5 Hz, C_{60}, 1 C), 65.46 (d, $^1J_{CP}$ = 32.4 Hz, C_{60}, 1 C), 125.30 (d, $^1J_{CP}$ = 50.2 Hz, C_6H_5, 2 C), 129.01 (d, $^2J_{CP}$ = 10.5 Hz, C_6H_5, 4 C), 132.54 (d, $^4J_{CP}$ = 2.9 Hz, C_6H_5, 2 C), 134.82 (d, $^3J_{CP}$ = 8.6 Hz, C_6H_5, 4 C), 135.79 (d, J_{CP} = 2.0 Hz, C_{60}, 2 C), 137.25 (d, J_{CP} = 4.8 Hz, C_{60}, 2 C), 139.20 (C_{60}, 2 C), 140.36 (C_{60}, 2 C), 141.20 (C_{60}, 2 C), 141.21 (C_{60}, 2 C), 141.36 (C_{60}, 2 C), 141.66 (C_{60}, 2 C), 141.77 (C_{60}, 2 C), 141.90 (C_{60}, 2 C), 142.04 (C_{60}, 2 C), 142.46 (C_{60}, 2 C), 142.64 (C_{60}, 2 C), 143.21 (C_{60}, 2 C), 144.22 (C_{60}, 2 C), 144.72 (C_{60}, 2 C), 145.32 (C_{60}, 2 C), 145.35(C_{60}, 2 C), 145.45 (C_{60}, 2 C), 145.67 (C_{60}, 2 C), 146.16 (C_{60}, 2 C), 146.24 (C_{60}, 2 C), 146.34 (C_{60}, 2 C), 146.40 (C_{60}, 2 C), 146.51 (C_{60}, 2 C), 146.54 (C_{60}, 2 C), 147.13 (C_{60}, 2 C), 147.23 (C_{60}, 1 C), 149.76 (d, J_{CP} = 4.8 Hz, C_{60}, 2 C), 152.54 (d, J_{CP} = 5.7 Hz, C_{60}, 2 C); ^{31}P NMR (162 MHz, $CS_2/CDCl_3$) 39.98; ^{11}B NMR (128 MHz, $CS_2/CDCl_3$) -58.74; FAB MS m/z 921 (M^++1), 720-724 (C_{60}); Anal. Calcd for $C_{72}H_{13}PB\cdot(CHCl_3)_{0.67}$: C, 87.23; H, 1.48. Found: C, 87.45; H, 1.75.

Methylphenyl(C_{60}H)phosphine-Borane 3b.

IR ($CHCl_3$) 3000, 2380, 1600, 1120, 1055, 525; ^{1}H NMR (500 MHz, $CS_2/CDCl_3$) 1.20-2.00 (br m, 3 H, BH_3), 2.47 (d, $^2J_{PH}$ = 9.2 Hz, 3 H, CH_3), 7.04 (d, $^3J_{P-H}$ = 24.8 Hz, 1 H, C_{60}H), 7.65-7.68 (m, 3 H, *m*- and *p*-C_6H_5), 8.22-8.26 (m, 2 H, *o*-C_6H_5); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) 7.60 (d, $^1J_{CP}$ = 36.2 Hz, CH_3), 57.19 (d, $^2J_{CP}$ = 11.5 Hz, C_{60}, 1 C), 64.01 (d, $^1J_{CP}$ = 31.5 Hz, C_{60}, 1 C), 124.95 (d, $^1J_{CP}$ = 49.6 Hz, C_6H_5, 1 C), 128.92 (d, $^2J_{CP}$ = 10.5 Hz, C_6H_5, 2 C), 132.82 (C_6H_5, 1 C), 133.92 (d, $^3J_{CP}$ = 8.6 Hz, C_6H_5, 2 C), 135.37 (d, J_{CP} = 1.9 Hz, C_{60}, 1 C), 135.70 (d, J_{CP} = 1.9 Hz, C_{60}, 1 C), 137.07 (d, J_{CP} = 2.9 Hz, C_{60} 1 C), 139.66 (d, J_{CP} = 3.8 Hz, C_{60}, 1

C), 140.33 (C_{60}, 1 C), 140.40 (C_{60}, 1 C), 141.36 (C_{60}, 3 C), 141.39 (C_{60}, 2 C), 141.54 (C_{60}, 2 C), 141.59 (C_{60}, 1 C), 141.62 (C_{60}, 1 C), 141.70 (C_{60}, 1 C), 141.73 (C_{60}, 1 C), 141.86 (C_{60}, 1 C), 141.97 (C_{60}, 2 C), 142.02 (C_{60}, 1 C), 142.47 (C_{60}, 2 C), 142.60 (C_{60}, 2 C), 143.16 (C_{60}, 1 C), 143.22 (C_{60}, 1 C), 144.18 (C_{60}, 1 C), 144.23 (C_{60}, 1 C), 144.66 (C_{60}, 1 C), 144.71 (C_{60}, 1 C), 145.30 (C_{60}, 1 C), 145.31 (C_{60}, 1 C), 145.42 (C_{60}, 2 C), 145.43 (C_{60}, 1 C), 145.44 (C_{60}, 1 C), 145.47 (C_{60}, 1 C), 145.59 (C_{60}, 1 C), 145.69 (C_{60}, 1 C), 146.12 (C_{60}, 1 C), 146.19 (C_{60}, 1 C), 146.22 (C_{60}, 1 C), 146.25 (C_{60}, 3 C), 146.29 (C_{60}, 1 C), 146.35 (C_{60}, 1 C), 146.36 (C_{60}, 1 C), 146.41 (C_{60}, 1 C), 146.57 (C_{60}, 1 C), 146.63 (C_{60}, 1 C), 147.14 (C_{60}, 1 C), 147.23 (C_{60}, 1 C), 148.93 (d, J_{CP} = 4.7 Hz, C_{60}, 1 C), 148.99 (d, J_{CP} = 4.7 Hz, C_{60}, 1 C), 152.06 (d, J_{CP} = 4.8 Hz, C_{60}, 1 C), 152.14 (d, J_{CP} = 4.8 Hz, C_{60}, 1 C); Anal. Calcd for $C_{67}H_{12}PB\cdot(CHCl_3)_{1.11}$: C, 82.54; H, 1.33. Found: C, 82.55; H, 1.32.

(*Sp*,1'*R*,2'*S*,5'*R*)-(2'-Isopropyl-5'-methylcyclohexyl)(C_{60}H)phenylphosphinite-Borane 7.

E*ox1* = +1.23, E*ox2* = +1.45, E*red1* = -1.21, E*red2* = -1.68, E*red3* = -2.12, E*red4* = -2.57 V (vs. Fc/Fc^+); IR ($CHCl_3$) 2955, 2920, 2390, 1600, 1460, 1440, 1115, 975, 530; ^1H NMR (400 MHz, $CS_2/CDCl_3$) 0.83-2.30 (m, 11 H), 0.87 (d, J = 6.4 Hz, 3 H, $CH(CH_3)_2$), 0.93 (d, J = 6.8 Hz, 3 H, CH_3), 1.02 (d, J = 6.6 Hz, 3 H, $CH(CH_3)_2$), 2.78-2.92 (m, 1 H, $CH(CH_3)_2$), 4.78-4.91 (m, 1 H, POC*H*), 7.17 (d $^3J_{P-H}$ = 26.0 Hz, 1 H, C_{60}H), 7.56 (ddd, J = 7.1, 6.4, 4.2 Hz, 1 H, *m*-C_6H_5), 7.57 (ddd, J = 8.8, 7.1, 4.2 Hz, 1 H, *m*-C_6H_5), 7.62 (dddt, J = 8.8, 6.4, 1.7, 1.4 Hz, 1 H, *p*-C_6H_5), 8.20 (ddd, J = 9.8, 7.1, 1.4 Hz, 2 H, *o*-C_6H_5); ^{31}P NMR (162 MHz, $CS_2/CDCl_3$) 118.36; ^{11}B NMR (128 MHz, $CS_2/CDCl_3$) -61.39; Anal. Calcd for $C_{76}H_{28}OPB\cdot(CHCl_3)_{1.13}$: C, 81.71; H, 2.59. Found: C, 81.55; H, 2.59.

(*Rp*,1'*R*,2'*S*,5'*R*)-(2'-Isopropyl-5'-methylcyclohexyl)(C_{60}H)phenylphosphinite-Borane 10.

IR ($CHCl_3$) 2950, 2925, 2375, 1435, 1110, 970, 525; ^1H NMR (400 MHz, $CS_2/CDCl_3$) 1.00-2.15 (m, 11 H), 0.62 (d, J = 6.8 Hz, 3 H, $CH(CH_3)_2$), 0.85 (d, J = 6.8 Hz, 3 H, CH_3), 0.96 (d, J = 6.3 Hz, 3 H, $CH(CH_3)_2$), 2.50-2.58 (m, 1 H, $CH(CH_3)_2$), 4.60-4.69 (m, 1 H, POC*H*), 7.00 (d, $^3J_{PH}$ = 26.0 Hz, 1 H, C_{60}H), 7.62-7.69 (m, 3 H, *m*- and *p*-C_6H_5), 8.27-8.33 (m, 2 H, *o*-C_6H_5); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) 15.30 (d, J_{CP}= 18.4 Hz), 20.98 (d, J_{CP}= 12.8 Hz), 22.14 (d, J_{CP} = 11.0 Hz), 22.76, 25.74, 31.77, 33.95, 44.05 (d, J_{CP} = 5.5 Hz), 48.91 (d, J_{CP} = 3.7 Hz), 56.62 (d, $^2J_{CP}$ = 12.9 Hz, C_{60}, 1 C), 68.67 (d, $^1J_{CP}$ = 42.3 Hz, C_{60} 1 C), 82.71 (d, $^2J_{CP}$ = 47.8 Hz, POC), 128.29 (d, $^3J_{CP}$ = 4.5 Hz, C_6H_5, 2 C), 128.57 (d, $^1J_{CP}$ = 55.1 Hz, C_6H_5, 1 C), 133.02 (C_6H_5, 1 C), 133.29 (d, $^2J_{CP}$ = 11.0 Hz, C_6H_5, 2 C), 135 39 (C_{60}, 1 C), 135.94 (C_{60}, 1 C), 136.95 (d, J_{CP} = 3.7 Hz, C_{60}, 1 C), 137.05 (d, J_{CP} = 5.5 Hz, C_{60}, 1 C), 139.22 (C_{60}, 1 C), 139.58 (C_{60}, 1 C), 140.31 (C_{60}, 2 C), 141.32 (C_{60}, 2 C), 141.39 (C_{60}, 1 C), 141.56 (C_{60}, 2 C), 141.65 (C_{60}, 1 C), 141.90 (C_{60}, 4 C), 141.98 (C_{60}, 1 C), 142.03 (C_{60}, 1 C), 142.45 (C_{60}, 1 C), 142.49 (C_{60}, 1 C), 142.58 (C_{60}, 2 C), 143.11 (C_{60}, 1 C), 143.15 (C_{60}, 1 C), 144.26 (C_{60}, 1 C), 144.34 (C_{60}, 1 C), 144.59 (C_{60}, 1 C), 144.65 (C_{60}, 1 C), 145.29 (C_{60}, 2 C), 145.32 (C_{60}, 1 C), 145.38 (C_{60}, 4 C), 145.45 (C_{60}, 1 C), 145.67 (C_{60}, 1 C), 145.75 (C_{60}, 1 C), 146.15 (C_{60}, 1 C), 146.24 (C_{60}, 2 C), 146.31 (C_{60}, 1 C), 146.37 (C_{60}, 2 C), 146.40 (C_{60}, 1 C), 146.79 (C_{60}, 2 C), 147.15 (C_{60}, 2 C), 147.37 (C_{60}, 1 C), 147.67 (C_{60}, 1 C), 149.15 (d, J_{CP} = 3.6 Hz, C_{60}, 1 C), 149.25 (d, J_{CP} = 5.5 Hz, C_{60}, 1 C), 152.03 (d, J_{CP} = 5.5 Hz, C_{60}, 1 C), 152.34 (d, J_{CP} = 5.5 Hz, C_{60}, 1 C); Anal. Calcd for $C_{76}H_{28}OPB\cdot(CHCl_3)_{0.4}$: C, 87.68; H, 2.73. Found: C, 87.69; H, 2.41.

Diphenyl(C_{60}H)phosphine 1.

To a solution of **3a** (92.1 mg, 0.1 mmol) in degassed toluene (60 mL) was added DABCO (223.4 mg, 2.0 mmol) at room temperature under nitrogen, and the resulting solution was stirred for 1.5 h. The reaction mixture was passed through a short column of silica gel (elution with degassed toluene) under nitrogen to give **1** (82.0 mg, 90%). An analytically pure sample was obtained by purification on a recycling preparative HPLC. E*red1* = -1.19, E*red2* = -1.54, E*red3* = -2.05 V (vs. Fc/Fc^+); IR ($CHCl_3$) 2910, 1490, 1090, 1020, 900, 520; ^1H NMR (500 MHz,

$CS_2/CDCl_3$ = 1/1) 6.82 (d, $^3J_{PH}$ = 15.6 Hz, 1 H, $C_{60}H$) 7.53-7.57 (m, 6 H, *m*- and *p*-C_6H_5), 8.23 (ddd, *J* = 9.2, 7.3, 1.4 Hz, 2 H, *o*-C6H5), 8.25 (ddd, J = 9.2, 7.3, 1.8 Hz, 2 H, *o*-C6H5); ^{31}P NMR (203 MHz, CS_2/CD_2Cl_2 = 1/1) 29.93; Anal. Calcd for $C_{72}H_{11}P\cdot(CHCl_3)_{0.08}$: C, 94.47; H, 1.22. Found: C, 94.47; H, 1.35.

(*S*P,1'*R*,2'*S*,5'*R*)-(2'-Isopropyl-5'-methylcyclohexyl)(C_{60}H)phenylphosphinite 8.

IR ($CHCl_3$) 2975, 2900, 1300, 930, 525; ^{1}H NMR (270 MHz, $CS_2/CDCl_3$) 0.80-1.80 (m, 8 H), 0.86 (brd, *J* = 5.9 Hz, 6 H, $CH(CH_3)_2$ and CH_3), 0.88 (d, *J* = 7.3 Hz, 3 H, $CH(CH_3)_2$), 2.82-2.95 (m, 1 H, $CH(CH_3)_2$), 4.27-4.29 (m, 1 H, POC*H*), 6.86 (d, $^3J_{PH}$ = 13.7 Hz, 1 H, $C_{60}H$), 7.47-7.54 (m, 3 H, *m*- and *p*-C_6H_5), 7.96-8.30 (m, 2 H, *o*-C_6H_5).

(*R*P,1'*R*,2'*S*,5'*R*)-(2'-Isopropyl-5'-methylcyclohexyl)(C_{60}H)phenylphosphinite 11.

IR ($CHCl_3$) 2950, 2910, 1020, 930, 520; ^{1}H NMR (270 MHz, $CS_2/CDCl_3$) 0.80-1.80 (m, 8 H), 0.82 (d, *J* = 7.3 Hz, 3 H, $CH(CH_3)_2$), 0.93 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.00 (d, *J* = 5.9 Hz, 3 H, $CH(CH_3)_2$), 2.65-2.75 (m, 1 H, $CH(CH_3)_2$), 4.09-4.22 (m, 1 H, POCH), 6.81 (d, $^3J_{PH}$ = 14.2 Hz, 1 H, $C_{60}H$), 7.52-7.60 (m, 3 H, *m*- and *p*-C_6H_5), 8.01-8.09 (m. 2 H, *o*-C_6H_5).

Reaction of 1 with BH_3•THF. Diphenyl(C_{60}H)phosphine-Borane Complex 3a.

To a solution of **1** (9.1 mg, 0.01 mmol) in 5 mL of degassed toluene was added BH_3•THF (10 μL, 1.0 M in THF, 0.01 mmol) at -72 °C, and the resulting solution was stirred for 0.5 h at this temperature. Removal of the solvent followed by purification by silica gel chromatography (silica gel: 1 g, elution with toluene) afforded **3a** in quantitative yield (9.2 mg, 0.01 mmol).

Oxidation of 1. Diphenyl(C_{60}H)phosphine Oxide 2.

To a solution of **1** (9.1 mg, 0.01 mmol) in toluene (6 mL) was added mCPBA (1.7 mg, 0.01 mmol) at 0 °C under nitrogen. After stirring for 10 min., sat. $Na_2S_2O_3$ and sat. $NaHCO_3$ was added. The organic layer was separated and aqueous layer was extracted with toluene. The combined organic extracts were washed with sat. NaCl and dried over Na_2SO_4. Removal of the solvent followed by purification by silica gel chromatography (silica gel 5 g, 8% EtOAc in toluene) afforded **2** as black powder (9.2 mg, 100%). An analytically pure sample was obtained by purification on a recycling preparative HPLC. IR ($CHCl_3$) 2975, 1710, 1600, 1440, 1185, 1115, 695, 615, 525; ^{1}H NMR (270 MHz, $CS_2/CDCl_3$) 7.10 (d, $^3J_{PH}$ = 25.9 Hz, 1 H, $C_{60}H$), 7.62-7.72 (m, 6 H, *m*- and *p*-C_6H_5), 8.48-8.56 (m, 4 H, *o*-C_6H_5); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) 57.02 (d, $^2J_{CP}$ = 7.4 Hz, C_{60}, 1 C), 70.81 (d, $^1J_{CP}$ = 30.3 Hz, C_{60}, 1 C), 128.82 (d, $^2J_{CP}$ = 12.4 Hz, C_6H_5, 4 C), 129.02 (d, $^1J_{CP}$ = 98.22, C_6H_5, 2 C), 132.94 (d, $^4J_{CP}$ = 2.9 Hz, C_6H_5, 2 C), 133.11 (d, $^3J_{CP}$ = 8.6 Hz, C_6H_5, 4 C), 135.56 (d, J_{CP} = 2.8 Hz, C_{60}, 2 C), 137.10 (d, J_{CP} = 4.7 Hz, C_{60}, 2 C), 139.61 (C_{60}, 2 C), 140.40 (C_{60}, 2 C), 141.36 (C_{60}, 2 C), 141.41 (C_{60}, 2 C), 141.66 (C_{60}, 2 C), 141.77 (C_{60}, 2 C), 141.99 (C_{60}, 2 C), 142.02 (C_{60}, 2 C), 142.48 (C_{60}, 2 C), 142.62 (C_{60}, 2 C), 143.21 (C_{60}, 2 C), 144.23 (C_{60}, 2 C), 144.66 (C_{60}, 2 C), 145.34 (C_{60}, 2 C), 14.39 (C_{60}, 2 C), 145.40 (C_{60}, 2 C), 145.41 (C_{60}, 2 C), 145.52 (C_{60}, 2 C), 145.72 (C_{60}, 2 C), 146.19 (C_{60}, 2 C), 146.26 (C_{60}, 2 C), 146.33 (C_{60}, 2 C), 146.43 (C_{60}, 2 C), 146.79 (C_{60}, 2 C), 147.13 (C_{60}, 1 C), 147.23 (C_{60}, 1 C), 149.34 (d, J_{CP} = 6.5 Hz, C_{60}, 2 C), 152.32 (d, J_{CP} = 4.8 Hz, C_{60}, 2 C); ^{31}P NMR (203 MHz, CS_2/CD_2Cl_2 = 1/1) 31.15. FAB MS m/z 922-925 (M^+), 720-724 (C_{60}); Anal. Calcd for $C_{72}H_{11}OP\cdot(CHCl_3)_{1.05}$: C, 83.71; H, 1.16. Found: C, 83.69; H, 0.97.

Dimethoxy(C_{60}H)phosphine-Borane 2c.

To a solution of dimethylphosphite (0.19 mL, 2.1 mmol) in 1.0 mL of THF was added a 1.50M BuLi in hexane (1.29 ml, 1.9 mmol) at -78C. After 45 min, the solution was transferred to a solution of C_{60} (499 mg, 0.69 mmol) in 360 mL of toluene at -78C. After 1 h, the cooling bath was removed and the reaction mixture was gradually warmed to room temperature. At room temperature, 5.0 mL of 0.4N HCl/EtOAc solution was added.

Filtration through a pad of silica gel afforded a solid weighing 425.1 mg. The crude product was purified by chromatography on silica gel (12g,30% EtOAc in toluene) to obtain C_{60} (186.4 mg, 37%) and the title compound (185.1 mg, 32%). *Eox1* = +1.16, *Eox2* = +1.39, *Ered1* = -1.16, *Ered2* = -1.52, *Ered3* = -1.93 V (vs. Fc/Fc^+); IR (CCl_4) 2950, 1635, 1540, 1488, 1386, 1260, 1053, 1028, 680, 528; ^1H NMR (400 MHz, $CS_2/CDCl_3$) 4.34 (d, ^3JHP = 29.8 Hz, 6 H, OCH_3), 7.22 (d, ^3JHP = 10.7 Hz, 1 H, $C_{60}H$); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) 55.21 (d, ^2JCP= 7.4 Hz, CH_3OP, 2 C), 56.33 (C_{60}, 1C), 65.23 (d, ^1JCP = 150.8Hz, C_{60}, 1 C), 135.30 (d, ^4JCP = 2.3Hz, C_{60}, 2 C), 136.23 (d, ^3JCP = 5.9Hz, C_{60}, 2 C), 140.24 (C_{60}, 2 C), 140.45 (C_{60}, 2 C), 141.34 (d, ^4JCP = 2.7 Hz, C_{60}. 2 C), 141.43 (C_{60}, 2 C), 141.61 (C_{60}, 2 C), 141.84 (C_{60}, 4 C), 141.87 (d, ^3JCP = 6.9Hz, C_{60}, 2 C), 142.47 (C_{60}, 2 C), 142.55 (C_{60}, 2 C), 143.13 (C_{60}, 2 C), 144.26(C_{60}, 2 C), 144.55 (C_{60}, 2 C), 145.28 (C_{60}, 2 C), 145.37 (C_{60}, 2 C), 145.44 (C_{60}, 2 C), 145.49(d, ^4JCP = 2.3Hz, C_{60}, 2 C), 145.72(C_{60}, 2 C), 146.15 (C_{60}, 2 C), 146.22(C_{60}, 2 C), 146.27 (C_{60}, 2 C), 146.37 (C_{60}, 2 C), 146.78 (C_{60}, 2 C), 147.09 (C_{60}, 1 C), 147.15 (C_{60}, 1 C), 147.29 (d, ^4JCP = 1.9 Hz, C_{60}, 2 C), 148.51(d, ^2JCP = 11.5 Hz, C_{60}, 2 C), 151.46 (d, ^3JCP = 6.4 Hz, C_{60}, 2 C).

Synthesis of $PtCl_2$•8_2.

To a solution of **7** (142 mg, 0.14 mg) in 70 mL of degassed toluene was added DABCO (1.57 g, 14 mmol) at room temperature, and the resulting solution was stirred for 4 h at this temperature. The mixture was passed through a pad of silica gel (silica gel: 20g, elution with degassed toluene), and $PtCl_2(PhCN)_2$ (33.1 mg, 0.07 mg) was added. The reaction mixture was stirred for 24 h at room temperature, and the solvent was removed to give a black powder (165 mg). An analytically pure sample of $PtCl_2$•8_2 was obtained by precipitation from $CHCl_3$ with hexane (brown powder). *Eox1* = +1.18, *Eox2* = +1.32, *Ered1* = -1.19, *Ered2* = -1.61, *Ered3* = -1.91, *Ered4* = -2.17, *Ered5* = -2.38 V (vs. Fc/Fc^+); IR ($CHCl_3$) 1602, 1507, 1459, 963, 530; ^1H NMR (500 MHz, $CS_2/CDCl_3$ = 1/1) 0.90 (d, J = 6.9 Hz, 3 H), 1.00 (d, J = 6.4 Hz, 3 H), 1.15 (d, J = 6.9 Hz, 3 H), 0.80-1.90 (series of m, 7 H), 2.70-2.85 (m, 1 H), 3.13 (d, J = 11.9 Hz, 1 H), 5.65-5.75 (m, 1 H), 7.48-7.60 (m, 3 H), 7.94 (t, J = 14.2 Hz, 1 H), 8.37-8.45 (m, 2 H); ^{31}P NMR (203 MHz, $CS_2/CDCl_3$ = 1/1) 92.71 ($J_{P\text{-}Pt}$ = 2900 Hz); Anal. Calcd for $C_{152}H_{50}O_2P_2PtCl_2$: C, 81.65; H, 2.25. Found: C, 81.46; H, 2.16.

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