washed sequentially with aqueous $NaHCO_3$, water, and brine, and dried (Na_2SO_4). The residue obtained by evaporation was subjected to column chromatography on silica gel (hexane/EtOAc 90/10) to furnish **7a** (144 mg, 98%).

Received: February 9, 1999 [Z13018IE]
German version: *Angew. Chem.* **1999**, *111*, 2397–2400

Keywords: arenes · eliminations · enones · integrated chemical process · one-pot reaction

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Electronic Communication in C_4-Bridged Binuclear Complexes with Paramagnetic Bisphosphane Manganese End Groups

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Dedicated to Professor Helmut Werner on the occasion of his 65th birthday

Binuclear metal complexes $[L_nMC_xML_n]$ bridged by linear unsaturated carbon chains are of exceptional interest as building blocks for new one-dimensional materials.[1] Electronic and optical properties of the molecular precursors, such as metal–metal interactions in mixed-valent compounds and electron delocalization and conjugation within the carbon chain, are important for the prediction and optimization of bulk properties of polymeric materials, such as nonlinear optical (NLO) properties,[2] electrical conductivity,[3] or cooperative magnetic effects.[4] Most complexes found in the literature possess an even number of carbon atoms in the chain ($x = 2$,[5] 4,[6] ≥ 6[7]), a few also an uneven number ($n = 3$,[8] 5[9]). The metal centers usually have a d^8/d^8, d^6/d^6, d^5/d^6, or d^5/d^5 electron configuration.[10] Paramagnetic complexes are supposed to be more polarizable, as their SOMO/LUMO gaps are usually small—an important prerequisite, for example, for NLO properties.[2] We report the syntheses, properties, and solid-state structures of the paramagnetic binuclear Mn^{II} compound **1** (dmpe = 1,2-bis(dimethylphosphanyl)ethane) and of its one- and two-electron oxidation products $\mathbf{1}^+$ and $\mathbf{1}^{2+}$, respectively.

$[I(dmpe)_2Mn{-}C{\equiv}C{-}C{\equiv}C{-}Mn(dmpe)_2I]$ **1**

According to Scheme 1 the green d^5 low-spin Mn^{II} complex **1** is obtained from [MeCpMn(dmpe)I][18a] and half an equivalent of bis(trimethylstannyl)-1,3-butadiyne in the presence of DMPE in 70% yield. The low-spin character of **1** is shown by ^{1}H PNMR spectroscopy: the resonances of the methyl and methylene protons of the DMPE ligand appear in a typical region for low-spin $[Mn^{II}(dmpe)_2]$ complexes (Figure 1).[11]

The linear dependence of the signal positions on the temperature points to Curie–Weiss behavior in the measured temperature range from $-90\,^\circ$C to $25\,^\circ$C. As theoretically predicted for the isolobal complex $[Cp(CO)_2Mn{-}C{\equiv}C{-}C{\equiv}C{-}Mn(CO)_2Cp]$[12] and confirmed by our density functional theory (DFT) calculations on the model complex $[I(PH_3)_4Mn{-}C{\equiv}C{-}C{\equiv}C{-}Mn(PH_3)_4I]$, **1** has a triplet ground state (Figure 2).[13]

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[**] This work was supported by the Swiss National Science Foundation (SNSF). We thank Dr. Vassily V. Krivykh for some synthetic explorations.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

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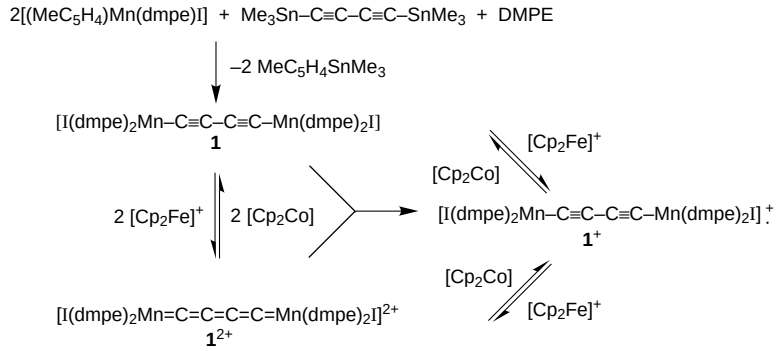


Scheme 1. Syntheses of the binuclear complexes **1**, $\mathbf{1}^+$, and $\mathbf{1}^{2+}$.

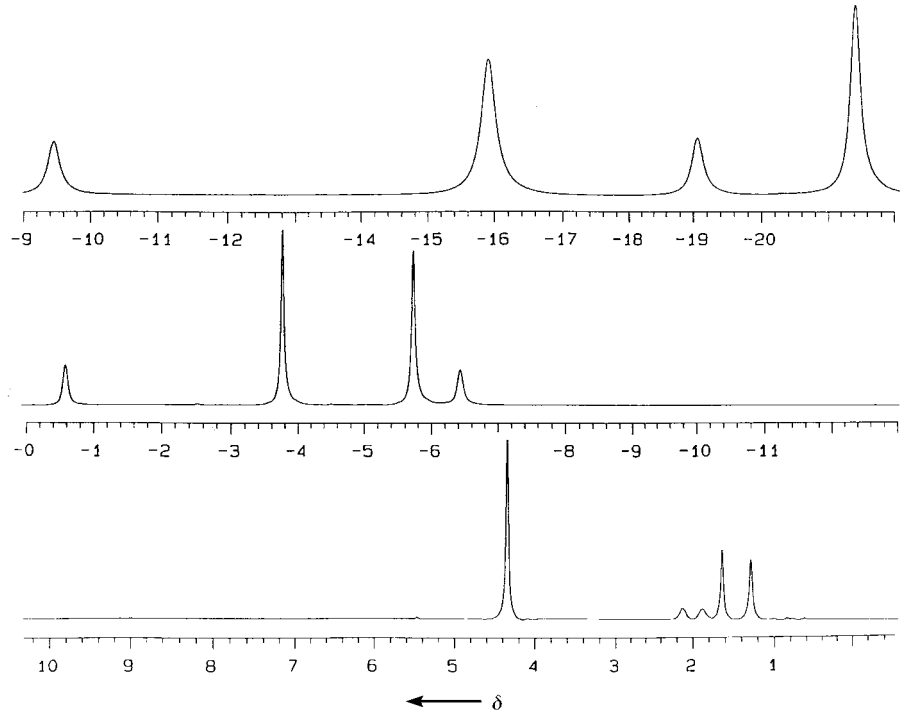


Figure 1. ^{1}H NMR spectra (25 °C) of the complexes **1** (top), **1**[PF_6] (middle) and **1**[PF_6]$_2$ (bottom).

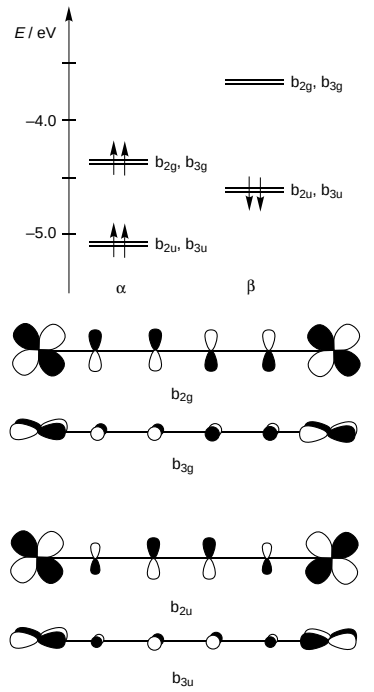
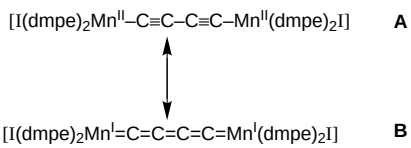


Figure 2. Frontier orbitals of the model complex [I(PH_3)$_4$Mn–C≡C–C≡C–Mn(PH_3)$_4$I] (in D_{2h} symmetry). Representation of the α- and β-spin separated orbitals. Pairs of practically degenerate b_2 and b_3 functions occur.



Scheme 2. Resonance structures for **1**.

The two electrons occupy practically degenerate, orthogonal π-molecular orbitals which extend over the C_4 chain and the manganese centers with parallel spins. This interpretation is confirmed by the ^{1}H PNMR spectra (Figure 1), as the signals are significantly paramagnetically shifted compared to those of complex $\mathbf{1}^+$, which should have only one unpaired electron (see below). In the electronic spectrum an intense absorption band is observed at 908 nm, probably corresponding to the lowest energy spin- and symmetry-allowed transition (Figure 2; $b_{2u}/b_{3u} \rightarrow b_{2g}/b_{3g}$). In the IR spectrum the $\tilde{\nu}_{C\equiv C}$ bands are found at 2127 and 1805 cm^{-1} confirming the description of the C_4 chain as a bis-acetylide (**A**) (Scheme 2). This is presumably also corroborated by the alternating C–C bond lengths found in the solid state, which however show for **1** relatively high standard deviations. Therefore some uncertainty in the given judgement remains (Scheme 3).[14] A small admixture of the cumulenic resonance formula **B** (Scheme 2) can be deduced from the smaller Mn–C and larger C≡C distances compared to those found in the complex *trans*-[(PhC≡C)$_2$Mn(dmpe)$_2$].[11a]

Cyclic voltammetry shows that **1** can be oxidized in two steps to the monocation $\mathbf{1}^+$ and the dication $\mathbf{1}^{2+}$, respectively.[15] The potential difference between these two redox processes of 0.63 V arises from strong exchange interactions between the manganese centers which are transmitted by the orbitals of the C_4 bridge. The thermodynamic stabilization of the mixed-valent compound $\mathbf{1}^+$ towards disproportionation into **1** and $\mathbf{1}^{2+}$ is confirmed by the large comproportionation constant[16] $K_C = 5.4 \times 10^{10}$. The one-dimensional C_4 chain in $\mathbf{1}^+$ evidently serves as a molecular wire to transmit the unpaired electron from one manganese center to the other. For similar C_4-bridged bimetallic complexes K_C values between 10^8 and 10^{12} were observed.[6]

Chemically, **1** can be oxidized with two equivalents of a ferrocinium salt to the red, diamagnetic dication $\mathbf{1}^{2+}$ (Scheme 1). In the ^{1}H NMR spectra the signals of the ligand protons appear in the diamagnetic region (Figure 1). The IR spectrum of $\mathbf{1}^{2+}$ shows a broad band at 1607 cm^{-1} ($\tilde{\nu}_{C=C}$ region) indicating that the C_4 chain is best described by the cumulenic resonance structure. Accordingly, in the solid state[14] almost equal C–C distances are observed for **1**[BPh_4]$_2$ (Scheme 3). For electron counting this would imply that the bridging ligand has been oxidized from the bis-acetylide to the

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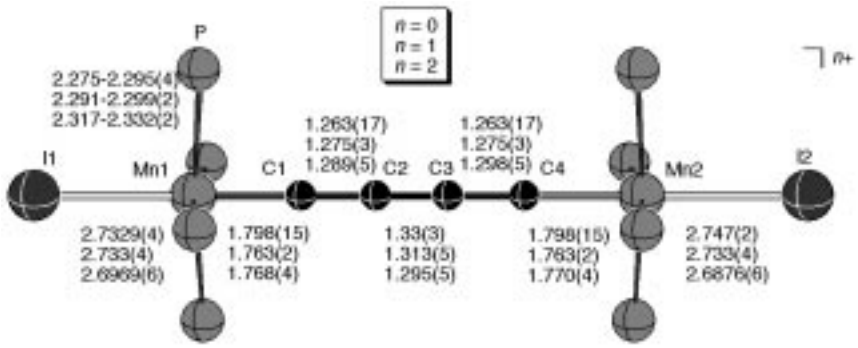

Scheme 3. Schematic drawing of the molecular structures of **1**, **1**[PF_6], and **1**[BPh_4]$_2$ (excluding counterions, solvent molecules; dmpe ligands shown as P).

cumulene leaving the metal oxidation number unaffected. In a molecular orbital description the relevant orbital extends over both metals and the ligand (Figure 2).

Comproportionation of **1** and $\mathbf{1}^{2+}$, oxidation of **1** or reduction of $\mathbf{1}^{2+}$ gives the blue mixed-valent complex $\mathbf{1}^{+}$ in almost quantitative yield. ^{1}H PNMR spectra confirm the paramagnetism and Curie–Weiss behavior of $\mathbf{1}^{+}$ in the temperature range from $-90\,^{\circ}$C to $+21\,^{\circ}$C. The fact that only *one* set of signals is observed for the protons of the DMPE ligands confirms that both end groups are equivalent on the NMR time scale (10^{-6} s). In the solid state **1**[PF_6] has a magnetic moment of 1.99 μ_B at 200 K, which drops to 1.66 μ_B at 5 K. This can be attributed to intermolecular antiferromagnetic interactions. In the EPR spectrum a broad feature without detectable hyperfine structure is observed at $g \approx 1.83$, in contrast to mononuclear low-spin [Mn(dmpe)$_2$] complexes,[11] leading to the interpretation that the system is in the fast exchange regime on the EPR time scale (10^{-9} s). In the IR spectrum the $\tilde{\nu}_{C\equiv C}$ absorptions are only marginally shifted relative to those of the neutral complex **1** (2123 and 1805 cm^{-1}). This demonstrates that the valencies are localized on the IR time scale (10^{-13} s) and therefore superimposed spectra of **1** (2127 and 1805 cm^{-1}) and $\mathbf{1}^{2+}$ (no $\tilde{\nu}_{C\equiv C}$ bands) are observed. The optical absorption spectra show intense charge-transfer bands at 378, 422, and 575 nm similar to the spectra of **1** and $\mathbf{1}^{2+}$; in the NIR spectrum an additional absorption band at approximately 1610 nm is found which has no counterpart in the spectra of **1** or $\mathbf{1}^{2+}$. Due to the low energy, the low intensity ($\varepsilon \approx 2470\,\mathrm{M^{-1}\,cm^{-1}}$), and the relatively large band width at half height ($\Delta\tilde{\nu}_{1/2} \approx 2070$ cm^{-1}), this band can be assigned to an intervalence transition.[16] The electronic coupling constant $H_{A,B}$ then amounts to about 500 cm^{-1} ($d_{Mn-Mn} \approx 7.4$ Å) and the rate constant for the thermal electron transfer to about $10^9 - 10^{10}$ s^{-1},[16] consistent with the interpretation of the EPR and IR data. The molecular structure of **1**[PF_6] in the solid state[14] has a center of symmetry, therefore both [Mn(dmpe)$_2$] fragments are crystallographically identical and are arranged perfectly eclipsed. The I-Mn-C-C-C-C-Mn-I chain is almost linear; the C–C bond lengths fall between those of **1** and $\mathbf{1}^{2+}$. Based on all spectroscopic data $\mathbf{1}^{+}$ can be described as a class II mixed-valent compound.[16]

With the synthesis of the complexes **1**, $\mathbf{1}^{+}$, and $\mathbf{1}^{2+}$ having two, one, and zero unpaired electrons, respectively, a further step towards a rational design of polymeric, one-dimensional, conducting or NLO-active materials has been made. Both the neutral complex **1** and the mixed-valent compound $\mathbf{1}^{+}$ possess half-filled energy levels enabling facile flow of electrons. This—extended to a polymeric structure—should lead to half-filled energy bands.[17] The complexes **1**, $\mathbf{1}^{+}$, and $\mathbf{1}^{2+}$ could be useful as building blocks for well-defined oligomers or polymers since their potential leaving group is expected to allow connection to further C_x chains.

Experimental Section

1: Under dinitrogen a solution of [MeCpMn(dmpe)I][18a] (0.411 g, 1.0 mmol) in THF (20 mL) was added to a solution of 1,4-bis(trimethylstannyl)-1,3-butadiyne[18b] (0.188 g, 0.5 mmol) in THF (10 mL) to give a dark violet solution. After 10 min 1,2-bis(dimethylphosphanyl)ethane[18c] (0.150 g, 1.0 mmol) in THF (5 mL) was added. After 45 min the solvent was removed, the remaining dark green solid was washed with pentane and dried in vacuo. Recrystallization from benzene/pentane at $-30\,^{\circ}$C gave green crystals of **1** (0.354 g, 0.35 mmol, 70 %). ^{1}H NMR (300 MHz, [D_8]toluene, 25 °C, TMS): $\delta = -21.35$ (br., 24 H, CH_3), -19.20 (br., 8 H, CH_2), -15.88 (br., 24 H, CH_3), -9.45 (br., 8 H, CH_2); ^{1}H NMR (300 MHz, [D_8]toluene, $-90\,^{\circ}$C, TMS): $\delta = -35.24$ (br., 24 H, CH_3), -31.08 (br., 8 H, CH_2), -25.05 (br., 24 H, CH_3), -16.16 (br., 8 H, CH_2); ^{31}P NMR (121.471 MHz, [D_8]toluene, 25 °C, 85 % H_3PO_4 (ext.)): $\delta = -50.0$ (br.); ^{31}P NMR (121.471 MHz, [D_8]toluene, $-80\,^{\circ}$C, 85 % H_3PO_4 (ext.)): $\delta = -49.3$ (s); IR (KBr): $\tilde{\nu} = 2127$ (s), 1805 (s) (C≡C), 940 (s), 927 (s) (P–C) cm^{-1}; UV/Vis/NIR (toluene): λ_{max} (ε) = 390 (40430), 504 (3820), 572 (4960), 908 (39360), 1164 (1400); ESR (toluene, 100 K): $g_{\perp} = 2.045$, $A_{\perp}(^{55}Mn) = 115$ G;[19] C,H analysis (%): calcd for $C_{28}H_{64}I_2Mn_2P_8$ (1012.297): C 33.22, H 6.37; found: C 33.37, H 5.99.

1[PF_6]$_2$: A solution of **1** (0.101 g, 0.10 mmol) and [Cp_2Fe][PF_6] (0.066 g, 0.20 mmol) in CH_2Cl_2 (20 mL) was stirred for 15 min under dinitrogen. The cherry red solution was filtered through a P4 frit, concentrated to 5 mL, and cold Et_2O was added. The precipitated solid was washed several times with Et_2O and dried in vacuo. Yield of **1**[PF_6]$_2$: 0.117 g, 0.09 mmol, 90 %. ^{1}H NMR (300 MHz, CD_3NO_2, 25 °C, TMS): $\delta = 1.30$ (br., 24 H, CH_3), 1.65 (br., 24 H, CH_3), 1.89 (br., 8 H, CH_2), 2.24 (br., 8 H, CH_2); ^{31}P NMR (121.471 MHz, CD_3NO_2, 21 °C, 85 % H_3PO_4 (ext.)): $\delta = -56.64$ (br., PCH_3), -144.77 (sept., $^1J_{P,F} = 714.11$ Hz, PF_6^-); ^{19}F NMR (282.324 MHz, CD_3NO_2, 30 °C, $C_6H_5CF_3$ (ext.)): $\delta = -74.04$ (d, $^1J_{P,F} = 714.28$ Hz, PF_6^-); IR (KBr): $\tilde{\nu} = 2017$ (w), 1607 (br.) (C=C), 948 (s), 933 (s) (P–C), 846 (s) (P–F) cm^{-1}; C,H analysis (%): calcd for $C_{28}H_{64}F_{12}I_2Mn_2P_{10}$ (1302.226): C 25.83, H 4.95; found: C 25.97, H 4.70.

1[BPh_4]$_2$: To a suspension of **1**[PF_6]$_2$ (0.052 g, 0.04 mmol) in CH_2Cl_2/THF (30 mL/10 mL) was added $NaBPh_4$ (0.027 g, 0.08 mmol), resulting in a clear cherry red solution. After 2 h the solution was filtered through a P4 frit, concentrated to 5 mL and cold Et_2O was added, giving copper red microcrystals. Recrystallization from CH_2Cl_2/THF gave **1**[BPh_4]$_2$ (0.060 g, 0.036 mmol, 90 %). IR (KBr): $\tilde{\nu} = 946$ (s), 930 (s) (P–C) cm^{-1}; UV/Vis/NIR (CH_2Cl_2): λ_{max} (ε) = 372 (15000), 404 (17100), 555 (30410), 688 (940, sh), 777 (430, sh), 997 nm (470, br.); CV (CH_3CN, [*n*BuN][PF_6], Ag/AgCl): $E_{1/2} = -0.020$ V (rev.), -0.655 V (quasirev.); C,H analysis (%): calcd for $C_{76}H_{104}B_2I_2Mn_2P_8$ (1650.773): C 55.29, H 6.35; found: C 55.37, H 6.01.

1[PF_6]: A solution of **1** (0.051 g, 0.05 mmol) and **1**[PF_6]$_2$ (0.065 g, 0.05 mmol) in CH_2Cl_2 (20 mL) was stirred for 15 h under dinitrogen. The deep blue solution was filtered over a P4 frit, concentrated to 5 mL, and cold Et_2O was added. The precipitated solid was washed several times with Et_2O and dried in vacuo. Recrystallization from CH_2Cl_2/Et_2O gave blue-violet **1**[PF_6] (0.104 g, 0.09 mmol, 90 %). ^{1}H NMR (300 MHz, CD_2Cl_2, 21 °C, TMS): $\delta = -6.46$ (br., 8 H, CH_2), -5.77 (br., 24 H, CH_3), -3.80 (br.,

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24H, CH_3), −0.65 (br., 8H, CH_2); ^{1}H NMR (300 MHz, CD_2Cl_2, −90 °C, TMS): δ = −11.13 (br., 8H, CH_2), −9.32 (br., 24H, CH_3), −3.68 (br., 24H, CH_3), −1.59 (br., 8H, CH_2); ^{31}P NMR (121.471 MHz, CD_2Cl_2, 21 °C, 85% H_3PO_4 (ext.)): δ = 42.99 (s, PCH_3), −144.77 (sept., $^1J_{P,F}$ = 714.11 Hz, PF_6^-); ^{19}F NMR (282.324 MHz, CD_2Cl_2, 21 °C, $C_6H_5CF_3$ (ext.)): δ = −74.40 (d, $^1J_{P,F}$ = 718.8 Hz, PF_6^-); IR (KBr): $\tilde{\nu}$ = 2123 (s), 1805 (w) (C≡C), 945 (s), 931 (s) (P–C), 842 (s) (P–F) cm^{-1}; UV/Vis/NIR (CH_2Cl_2): λ_{max} (ε) = 378 (56280), 422 (50450), 575 (45480), 773 (4920) 997 (720), 1610 nm (2470); μ_{eff} = 1.99 μ_B (200 K), 1.82 μ_B (100 K), 1.66 μ_B (5 K); ESR (CH_2Cl_2, 100 K): $g \approx 1.83$; C,H analysis (%): calcd for $C_{28}H_{64}F_6I_2Mn_2P_9$ (1157.298): C 29.06, H 5.57; found: C 29.31, H 5.27.

Received: March 8, 1999 [Z13129IE]
German version: *Angew. Chem.* **1999**, *111*, 2412 – 2415

Keywords: alkynyl complexes · electron transfer · manganese · metal – metal interactions · mixed-valent compounds

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[14] Crystal structure data: **1**: monoclinic, $P2_1/n$; a = 9.101(1), b = 17.387(2), c = 14.025(2) Å, β = 102.69(2), Z = 4, 3945 independent reflections ($Mo_{K\alpha}$; $2\theta_{max}$ = 52°); R = 0.0662, R_w = 0.1520 ($I = 2\sigma(I)$). **1**$[BPh_4]_2$: monoclinic, $P2_1/c$; a = 25.418(1), b = 12.5041(8), c = 29.465(1) Å, β = 113.931(5), Z = 4, 19875 independent reflections ($Mo_{K\alpha}$; $2\theta_{max}$ = 56°); R = 0.0438, R_w = 0.0730 ($I = 2\sigma(I)$). **1**$[PF_6]$: tetragonal, $I4cm$; a = 16.336(1), c = 17.738(2) Å, Z = 4, 2959 independent reflections ($Mo_{K\alpha}$; $2\theta_{max}$ = 56°); R = 0.0275, R_w = 0.0546 ($I = 2\sigma(I)$). STOE-IPDS diffractometer, T = 193 K, solution and refinement with the programs SHELXS-97 and SHELXL-97.[20] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-118429 (**1**), CCDC-118430 (**1**$[PF_6]$), and CCDC-118431 (**1**$[BPh_4]_2$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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