those of isoelectronic *trans*-$[\mathrm{OsO_2(CN)_4}]^{2-}$,[12, 25] but also with those of the homoleptic carbonyl cations $[\mathrm{Os(CO)_6}]^{2+}$[5] and, particularly, square-planar $[\mathrm{Pt(CO)_4}]^{2+}$.[17, 22]

The new superelectrophilic[26] cation *trans*-$[\mathrm{OsO_2(CO)_4}]^{2+}$ is unusual for two reasons:

1) It is the first oxo derivative of a homoleptic metal carbonyl cation. *trans*-$[\mathrm{OsO_2(CO)_4}]^{2+}$ joins a small but growing group of cations such as $[\mathrm{M(CO)_5Cl}]^{2+}$ (M = Rh, Ir),[27] $[\mathrm{W(CO)_6(FSbF_5)}]^{+}$,[28] and polymeric $[\{\mathrm{Mo(CO)_4}\}_2(\mathrm{cis}\text{-}\mu\text{-}\mathrm{F_2SbF_4})_3]^{+}$.[29] All are generated in superacids, have been structurally characterized, and have $[\mathrm{Sb_2F_{11}}]^{-}$ as counterion. With a number of superacidic media[1, 2] and very versatile synthetic routes available,[3] it should be possible to add more cationic derivatives with the atoms N, O, or F as ligands to this list.

2) *trans*-$[\mathrm{OsO_2(CO)_4}]^{2+}$ is the first cationic metal carbonyl complex with the metal in the formal oxidation state +6. Previously the highest oxidation state of the central metal was +4. Examples include the matrix molecule $[\mathrm{WO_2(CO)_4}]$[20] and the pentahalo-monocarbonyl-metalate(IV) anions $[\mathrm{PtCl_5(CO)}]^{-}$,[30], $[\mathrm{OsCl_5(CO)}]^{-}$,[31] and $[\mathrm{OsF_5(CO)}]^{-}$.[32]

Experimental Section

A 50-mL glass flask fitted with a PTFE valve and a magnetic stirring bar was dried by heating in vacuo and charged with $\mathrm{OsO_4}$ (0.116 g, 0.46 mmol). $\mathrm{SbF_5}$ (6.34 g, 20 mmol) was added by condensation in vacuo, and the CO pressure was adjusted to 1.5 bar (3.3 mmol). The initially clear solution was vigorously stirred at room temperature. After several days the solution became turbid, and after 10 days a yellow suspension formed. At room temperature all volatile components were removed in vacuo, and a finely powdered, yellowish solid (0.612 g) was obtained. Vibrational bands observed below 800 $\mathrm{cm^{-1}}$: IR: $\tilde{\nu}$ = 760 (m), 704 (vs), 655 (vs), 601 (m), 490 (sh), 407 (m), 346 (m), 311 (s), 276 (s), 240 (vs); Raman: 675 (vs), 645 (m), 605 (m), 296 (s), 232 (m) $\mathrm{cm^{-1}}$.

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A Facile Route to Group 13 Difluorodiorganometalates: $[n\mathrm{Bu_4N}][\mathrm{R_2MF_2}]$ (M = Al, Ga, In)**

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Dedicated to Professor Armin de Meijere
on the occasion of his 60th birthday

Group 13 difluorodiorganometalates have been known since 1955;[1] however, only a few of these were spectroscopically and structurally characterized.[2] Furthermore, the synthesis of these anions was not straightforward. We describe herein the synthesis, X-ray crystal structure,[3] and NMR and IR spectroscopic characterization of some difluorodiorganometalates $[n\mathrm{Bu_4N}][\mathrm{R_2MF_2}]$ (M = Al, Ga, In). The synthesis of these compounds is accomplished through protonolysis of trialkyl derivatives of Group 13 metals with tetra-*n*-butylammonium hydrogen difluoride (TBADF) at room temperature,[4] which induces elimination of methane and addition of two fluoride ions. The compounds **1**–**4** are obtained as colorless, rhombic crystals (Scheme 1).

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$$\mathrm{RMMe_2} + [n\mathrm{Bu_4N}][\mathrm{HF_2}] \xrightarrow[\text{- MeH}]{\text{THF, 20 °C}} [n\mathrm{Bu_4N}][\mathrm{RMeMF_2}]$$

M = Al, Ga, In

1: M = Al R = Me
2: M = Al R = Tris
3: M = Ga R = Me
4: M = In R = Me

Scheme 1. Synthesis of **1**–**4**. Tris = $(Me_3Si)_3C$.

Compounds **1**, **3**, and **4** are isomorphous and crystallize in the monoclinic space group $P2_1/n$ (Figure 1). Compound **2** crystallizes in the monoclinic space group $P2_1/c$ (Figure 2). The metal center of these anions has a distorted tetrahedral coordination environment. The average Al–F bond length in **1** (1.712 Å) and **2** (1.690 Å) is somewhat longer than normal Al–F single bonds (1.65 Å). The C-Al-C bond angle of **2** is nearly identical to that of **1** despite the presence of a more sterically demanding ligand in **2**; in addition, the F-Al-F bond angle is actually larger in **2** (106.0°) than in **1** (103.23°). The bond lengths and angles for **3** (Ga–F 1.838 and 1.839 Å, F-Ga-F 98.74°, C-Ga-C 125.1°) are similar to those obtained for $Cs[Me_2GaF_2]$[2] (Ga–F 1.827 and 1.838 Å, F-Ga-F 96.7°, C-Ga-C 127.8°). The average In–F bond length in **4** is 2.044 Å, and the F-In-F and C-In-C bond angles are 95.68° and 132.09°, respectively.

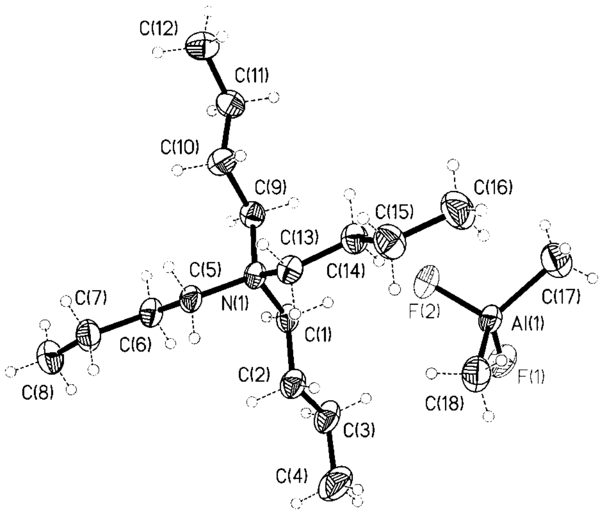

Figure 1. Molecular structure of **1**. Compounds **3** and **4** are isomorphous. Selected bond lengths [Å] and angles [°]. **1**: Al(1)–F(1) 1.7109(13), Al(1)–F(2) 1.7130(13), Al(1)–C(17) 1.965(2), Al(1)–C(18) 1.972(2); F(1)-Al(1)-F(2) 103.23(7), F(1)-Al(1)-C(17) 108.60(10), F(2)-Al(1)-C(17) 108.64(9), F(1)-Al(1)-C18 108.74(9), F(2)-Al(1)-C(18) 109.60(8), C(17)-Al(1)-C(18) 117.13(10); **3**: Ga(1)–F(2) 1.838(2), Ga(1)–F(1) 1.839(2), Ga(1)–C(18) 1.966(4), Ga(1)–C(17) 1.972(4); F(2)-Ga(1)-F1 98.74(10), F(2)-Ga(1)-C(18) 107.2(2), F(1)-Ga(1)-C(18) 108.27(14), F(2)-Ga(1)-C(17) 107.4(2), F(1)-Ga(1)-C(17) 107.0(2), C(18)-Ga(1)-C(17) 125.1(2); **4**: In(1)–F(1) 2.040(2), In(1)–F(2) 2.047(2), In(1)–C(18) 2.148(4), In(1)–C(17) 2.152(4); F(1)-In(1)-F(2) 95.68(8), F(1)-In(1)-C(18) 105.61(13), F(2)-In(1)-C(18) 105.47(15), F(1)-In(1)-C(17) 106.71(12), F(2)-In(1)-C(17) 105.45(14), C(18)-In(1)-C(17) 132.09(15).

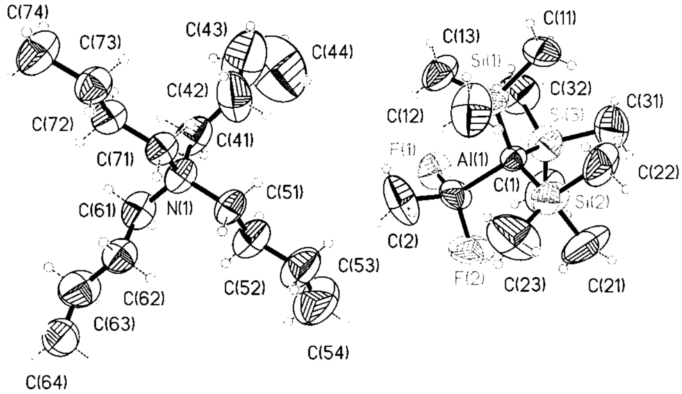

Figure 2. Molecular structure of **2**. Selected bond lengths [Å] and angles [°]: Al(1)–F(2) 1.680(5), Al(1)–F(1) 1.702(5), Al(1)–C(2) 1.945(11), Al(1)–C(1) 2.010(6); F(2)-Al(1)-F(1) 106.0(3), F(2)-Al(1)-C(2) 106.4(5), F(1)-Al(1)-C(2) 107.0(4), F(2)-Al(1)-C(1) 109.0(3), F(1)-Al(1)-C(1) 110.6(3), C(2)-Al(1)-C(1) 117.2(4).

The signals in the ^{19}F NMR spectra occur at $\delta = -154.8$ ($[D_8]THF$) for **1** and $\delta = -145.9$ (C_6D_6) for **2** as expected. Compound **3** displays a singlet at $\delta = -164.8$ (CD_3CN), while the signal for $Cs[Me_2GaF_2]$ occurs at $\delta = -149.6$ (CD_3CN). The signal in the ^{19}F NMR spectrum for **4** is observed at $\delta = -180.9$. As expected, the ^{19}F NMR resonances shift progressively to higher field in the series Al, Ga, In. The ^{27}Al NMR signal for **1** ($\delta = 123.8$) is typical for four-coordinate aluminum compounds. The ^{27}Al NMR resonance can be resolved as a triplet ($J = 120$ Hz) after Gaussian multiplication.

Compounds **1**–**4** all produce the expected signals of the metalates in the FAB (negative-ion) mass spectrum next to the signals for the matrix (3-nitrobenzyl alcohol (NBA)). The IR spectrum for **1** shows two absorptions at 742 and 651 cm^{-1}, attributable to Al–F bond stretches. The comparable bands for **3** occur at 518 and 494 cm^{-1}, while those for **4** are found at 450 and 430 cm^{-1}. Within the group (Al, Ga, In), the frequency of the metal–fluorine bond stretches decreases as expected.

While **1** reacts with water with evolution of gas, **3** and **4** are stable to moisture and exhibit no decomposition upon exposure to water. After an excess of D_2O was added, no decomposition could be detected after one day, as observed by the ^1H NMR signals for the methyl groups on the metal center. In contrast, $Cs[Me_2GaF_2]$ was reported to be sensitive to hydrolysis.[2]

The fluoride transfer with TBADF is simple to carry out, and has also been demonstrated with the fluorination of trisubstituted silanes.[5] This might also be extended to organotransition metal compounds.

Experimental Section

All manipulations were performed under a dry and oxygen-free nitrogen atmosphere. Glassware was heated and cooled under vacuum. Solvents were dried by appropriate methods, saturated with nitrogen, and freshly distilled. Gas evolution was measured by a mercury manometer. Melting points were determined with capillaries sealed under nitrogen and are not corrected.

1: A solution of TBADF (1.09 g, 3.86 mmol) in THF (4 mL) was added dropwise to a solution of $AlMe_3$ (1.95 g of a 15% solution in hexane, 4.06 mmol) in THF (5 mL) at room temperature, and the mixture was stirred for 30 min. Crystallization at −24 °C for two weeks yielded 1.16 g (3.44 mmol, 89%) of **1** as rhombic crystals. M.p. 90 °C; ^1H NMR (250 MHz, $[D_8]THF$, TMS): $\delta = -1.25$ (t, $J = 2.4$ Hz, 6H, $AlCH_3$), 1.00 (t, $J = 7.3$ Hz, 12H, CH_3), 1.41 (qt, $J = 7.5$ Hz, 8H, $C^{3/7/11/15}H_2$), 1.71 (tt, $J = 7.5$ Hz, 8H, $C^{2/6/10/14}H_2$), 3.35 (m, 8H, $C^{1/5/9/13}H_2$); ^{13}C NMR (126 MHz, $[D_8]THF$, TMS): $\delta = -10$ to -9.5 (br, $AlCH_3$), 14.01 (CH_3), 20.56 ($C^{3/7/11/15}H_2$), 24.69 ($C^{2/6/10/14}H_2$), 59.19 ($C^{1/5/9/13}H_2$); ^{19}F NMR (235 MHz, $[D_8]THF$, $CFCl_3$): $\delta = -154.82$ (s); ^{27}Al NMR (65.2 MHz, CD_3CN, $AlCl_3$): $\delta = 123.8$ (s, $W_{1/2} =$

327 Hz, after Gaussian multiplication: t, $J = 120$ Hz); IR (KBr, nujol): $\tilde{\nu} = 1571, 1491, 1308, 1261, 1172, 1154, 1095, 887, 802, 742, 651, 466$ cm^{-1}; MS (EI): m/z (%): 242 (17, Bu_4N), 142 (100, Bu_2NCH_2); negative-ion FAB-MS (NBA matrix): m/z (%): 95 (70, Me_2AlF_2); elemental analysis calcd for $C_{18}H_{42}AlF_2N$ (337.51): C 64.1, H 12.5, N 4.2; found: C 62.8, H 12.1, N 4.2.

2: A solution of $TrisAlMe_2 \cdot THF$ (3.00 g, 8.32 mmol) was added dropwise to a solution of TBADF (2.34 g, 8.32 mmol) in THF (40 mL) at room temperature, and the mixture was stirred for 12 h. The solvent was removed in vacuo, and the residue was redissolved in toluene (30 mL). The solution was then filtered, and recrystallization at 0 °C for 3 d yielded 4.20 g (7.00 mmol, 84 %) of **2** as rhombic crystals. M.p. 108 °C; ^1H NMR (200 MHz, C_6D_6, TMS): $\delta = -0.29$ (t, $J = 2.8$ Hz, 3 H, $AlCH_3$), 0.69 (s, 27 H, Me_3Si), 0.91 (t, $J = 6.5$ Hz, 12 H, CH_3), 1.12–1.31 (m, 16 H, $C^{3/7/11/15}H_2$, $C^{2/6/10/14}H_2$), 2.91 (m, 8 H, $C^{1/5/9/13}H_2$); ^{19}F NMR (235 MHz, C_6D_6, $CFCl_3$): $\delta = -145.93$ (s); ^{29}Si NMR (79.5 MHz, C_6D_6, TMS): $\delta = -3.71$ (t, $J = 1.5$ Hz, Me_3Si); IR (KBr): $\tilde{\nu} = 2965, 2898, 2878, 1488, 1466, 1382, 1243, 1179, 1029, 869, 787, 754, 741, 709, 680, 664, 640, 575, 316$ cm^{-1}; EI-MS: m/z (%): 242 (100, Bu_4N), 100 (4, $Bu(Me)NCH_2$); negative-ion FAB-MS (NBA matrix): m/z (%): 311 (100, $Tris(Me)AlF_2$), 231 (9, Tris); elemental analysis calcd for $C_{30.5}H_{70}AlF_2NSi_3$ (600.13; crystallized with 0.5 molecules of C_7H_8): C 61.0, H 11.8, Al 4.5, F 6.3, N 2.3; found: C 61.8, H 11.5, Al 3.4, F 5.5, N 2.8.

3: $GaMe_3$ (1.71 g, 14.9 mmol) was cooled to −196 °C, and THF (10 mL) was added. The solution was warmed to −30 °C, and a solution of TBADF (4.08 g, 14.5 mmol) in THF (10 mL) was added dropwise. The mixture was then stirred for 30 min. Crystallization at 4 °C for 3 d yielded 4.35 g (11.4 mmol, 79 %) of **3** as rhombic crystals. M.p. 132 °C; ^1H NMR (500 MHz, CD_3CN, TMS): $\delta = -0.74$ (s, 6 H, $GaCH_3$), 0.96 (t, $J = 7.3$ Hz, 12 H, CH_3), 1.34 (qt, $J = 7.5$ Hz, 8 H, $C^{3/7/11/15}H_2$), 1.60 (tt, $J = 7.5$ Hz, 8 H, $C^{2/6/10/14}H_2$), 3.09 (m, 8 H, $C^{1/5/9/13}H_2$); ^{13}C NMR (126 MHz, CD_3CN, TMS): $\delta = -6.63$ (s, $GaCH_3$), 13.80 (CH_3), 20.35 ($C^{3/7/11/15}H_2$), 24.42 ($C^{2/6/10/14}H_2$), 59.36 ($C^{1/5/9/13}H_2$); ^{19}F NMR (235 MHz, CD_3CN, $CFCl_3$): $\delta = -164.76$ (s); IR (KBr, nujol): $\tilde{\nu} = 1576, 1494, 1261, 1181, 1152, 1109, 1024, 887, 802, 563, 518, 494$ cm^{-1}; EI-MS: m/z (%): 242 (34, Bu_4N), 142 (100, Bu_2NCH_2), 101 (19, Me_2Ga), 99 (29, Me_2Ga); negative-ion FAB-MS (NBA matrix): m/z (%): 139 (25, Me_2GaF_2), 137 (38, Me_2GaF_2); elemental analysis calcd for $C_{18}H_{42}F_2GaN$ (380.25): C 56.9, H 11.1, Ga 18.3, N 3.7; found: C 57.0, H 10.6, Ga 18.3, N 3.7.

4: A solution of TBADF (0.931 g, 3.31 mmol) in THF (5 mL) was added dropwise to a solution of $InMe_3$ (1.06 g of a 50 % solution in diethyl ether, 3.30 mmol) in THF (5 mL) at room temperature. A white precipitate formed immediately upon the addition of the TBADF and subsequently redissolved upon further addition of TBADF. The mixture was stirred for 30 min after the addition was complete. Crystallization at room temperature for 3 h yielded 0.470 g (1.10 mmol, 33 %) of **4** as rhombic crystals. M.p. 147 °C; ^1H NMR (500 MHz, [D$_8$]THF, TMS): $\delta = -0.56$ (s, 6 H, $InCH_3$), 0.99 (t, $J = 7.4$ Hz, 12 H, CH_3), 1.41 (qt, $J = 7.4$ Hz, 8 H, $C^{3/7/11/15}H_2$), 1.73 (tt, $J = 7.5$ Hz, 8 H, $C^{2/6/10/14}H_2$), 3.47 (m, 8 H, $C^{1/5/9/13}H_2$); ^{13}C NMR (126 MHz, [D$_8$]THF, TMS): $\delta = -7.35$ (br, $InCH_3$), 14.08 (CH_3), 20.66 ($C^{3/7/11/15}H_2$), 24.84 ($C^{2/6/10/14}H_2$), 59.22 ($C^{1/5/9/13}H_2$); ^{19}F NMR (235 MHz, [D$_8$]THF, $CFCl_3$): $\delta = -180.87$ (s); IR (KBr, nujol): $\tilde{\nu} = 1582, 1495, 1306, 1262, 1153, 1144, 1107, 1053, 1025, 888, 803, 738, 693, 507, 450, 430$ cm^{-1}; EI-MS: m/z (%): 242 (50, Bu_4N), 142 (100, Bu_2NCH_2), 115 (14, In); negative-ion FAB-MS (NBA matrix): m/z (%): 183 (18, Me_2InF_2); elemental analysis calcd for $C_{18}H_{42}F_2InN$ (425.35): C 50.8, H 9.9; found: C 50.8, H 9.6.

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[3] Crystal structure analysis: The data were collected on a Stoe Siemens four-circle diffractometer with $Mo_{K\alpha}$ radiation on rapidly cooled crystals suspended in oil with profile optimized $2\theta/\omega$ scans. The structures were solved using direct methods (SHELXS-97) and refined on F^2 (SHELXL-97).[6] A psi-scan absorption correction was used for **3** and **4**. – **1**: $C_{18}H_{42}AlF_2N$, $M_r = 337.51$, monoclinic, space group $P2_1/n$, $a = 10.744(2)$, $b = 12.124(2)$, $c = 17.203(3)$ Å, $\beta = 96.09(3)^\circ$, $V = 2228.1(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.006$ Mg m^{-3}, $F(000) = 752$, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 0.105$ mm^{-1}, $T = -123$ °C, crystal size $0.7 \times 0.7 \times 0.2$ mm^3. Of the 9616 reflections collected ($7.0 \leq 2\theta \leq 50.0^\circ$), 3921 were independent; max./min. residual electron density 237/−187 e nm^{-3}, $R1 = 0.0431$ ($I > 2\sigma(I)$) and $wR2 = 0.1187$ (all data). – **2**: $C_{30.5}H_{70}AlF_2NSi_3$ (including 0.5 molecules of toluene), $M_r = 600.13$, monoclinic, space group $P2_1/c$, $a = 17.618(3)$, $b = 12.917(2)$, $c = 17.681(3)$ Å, $\beta = 101.32(2)^\circ$, $V = 3945.1(12)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.010$ Mg m^{-3}, $F(000) = 1332$, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 0.170$ mm^{-1}, $T = -60$ °C, crystal size $0.8 \times 0.8 \times 0.6$ mm^3. Of the 9891 reflections collected ($7.0 \leq 2\theta \leq 45.0^\circ$), 5134 were independent; max./min. residual electron density 1373/−426 e nm^{-3}, $R1 = 0.1204$ ($I > 2\sigma(I)$), $wR2 = 0.3726$ (all data). – **3**: $C_{18}H_{42}F_2GaN$, $M_r = 380.25$, monoclinic, space group $P2_1/n$, $a = 10.8088(11)$, $b = 12.0465(11)$, $c = 17.336(2)$ Å, $\beta = 96.73(1)^\circ$, $V = 2241.7(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.127$ Mg m^{-3}, $F(000) = 824$, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 1.241$ mm^{-1}, $T = -70$ °C, $0.7 \times 0.6 \times 0.2$ mm^3. Of the 3265 reflections collected ($7.0 \leq 2\theta \leq 45.0^\circ$), 2924 were independent; max./min. residual electron density 499/−387 e nm^{-3}, $R1 = 0.0398$ ($I > 2\sigma(I)$), $wR2 = 0.1156$ (all data). – **4**: $C_{18}H_{42}F_2InN$, $M_r = 425.35$, monoclinic, space group $P2_1/n$, $a = 10.8943(12)$, $b = 11.984(2)$, $c = 17.483(3)$ Å, $\beta = 96.20(1)^\circ$, $V = 2269.2(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.245$ Mg m^{-3}, $F(000) = 896$, $\lambda = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 1.055$ mm^{-1}, $T = -70$ °C, crystal size $0.90 \times 0.80 \times 0.40$ mm^3. Of the 6863 reflections collected ($7.0 \leq 2\theta \leq 45.0^\circ$), 3985 were independent; max./min. residual electron density 666/−722 e nm^{-3}, $R1 = 0.0371$ ($I > 2\sigma(I)$), $wR2 = 0.0960$ (all data). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-127535 (**1**), -127536 (**2**), -127537 (**3**), -127538 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Palladium-Catalyzed Intermolecular Controlled Insertion of Benzyne-Benzyne-Alkene and Benzyne-Alkyne-Alkene—Synthesis of Phenanthrene and Naphthalene Derivatives

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Alkynes are frequently used as a substrate for the transition metal catalyzed inter- and intramolecular carbometalation reaction.[1] However, arynes have hardly been utilized in transition metal catalyzed organic synthesis, although stoichiometric reactions of zirconium–benzyne and nickel–benzyne complexes were studied.[2] Quite recently, Castedo and his co-workers reported the efficient palladium-catalyzed cyclotrimerization of arynes[3a] and cocyclization of arynes with alkynes.[3b] During our continuing studies on the catalytic

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