steric encumbrance at this site and the fact that an S_N2-type attack on the cyclopropyl carbon C(3) has to pass through a highly strained transition structure.[15] The formation of complex **20** from **18** also shows that the attack at least of nitrogen nucleophiles on π-allylpalladium intermediates of type **8** must be reversible.

In conclusion, this new three-component reaction bears a significant combinatorial potential in that all three components may be varied just as in the previously described domino Heck–Diels–Alder sequence,[2] leading to a three-dimensional library of small molecules.

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[8] Representative procedure: 1-Cyclopropylidene-1-phenyl-2-morpholinopropane (**15i**): Morpholine (**14i**) (261 mg, 3.00 mmol) was added to a solution containing $Pd(OAc)_2$ (11.2 mg, 50.0 μmol; 5 mol%), TFP (23.2 mg, 100 μmol; 10 mol%), iodobenzene (**2**) (204 mg, 1.00 mmol), and bicyclopropylidene (**1**) (160 mg, 2.00 mmol) in DMF (0.5 mL), and the mixture was stirred for 1.5 h at 80 °C. After cooling to room temperature, the solution was added to water (10 mL), the mixture extracted with diethyl ether (5 × 20 mL), and the combined organic phases dried ($MgSO_4$). After removal of the solvent in a rotatory evaporator the residue was chromatographed on silica gel (25 g, column 2 × 20 cm, pentane/diethyl ether 5/1) to yield **15i** (240 mg, 99%) as a yellowish oil, $R_f = 0.55$. IR (film): $\tilde{\nu} = 3052, 2971, 2851, 2805$ (C–N), 1598, 1494, 1447, 1373, 1261, 1118, 1071, 926, 762, 698 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 1.21-1.43$ (m, 4H; *c*Pr-H), 1.28 (d, $^3J = 6.7$ Hz, 3H; 3-H), 2.42–2.63 (m, 4H; CH_2NCH_2), 3.58 (q, $^3J = 6.7$ Hz, 1H; 2-H), 3.69–3.78 (m, 4H; CH_2OCH_2), 7.23 (dd, $^3J = 7.0$, $^4J = 1.1$ Hz, 1H; 4′-H), 7.32 (dd, $^3J = 7.0$, $^3J = 7.2$ Hz, 2H; 3′-H, 5′-H), 7.82 (dd, $^3J = 7.2$, $^4J = 1.1$ Hz, 2H; 2′-H, 6′-H); ^{13}C NMR (62.9 MHz, $CDCl_3$, DEPT): $\delta = 2.74$ (–, *c*Pr-C), 3.74 (–, *c*Pr-C), 15.77 (+, C-3), 50.73 (–, C-2″, C-6″), 64.99 (+, C-2), 67.36 (–, C-3″, C-5″), 123.76 (C_{quat}, *c*Pr-C), 126.35 (+, C-4′), 127.23 (+, Ar-C), 127.77 (+, Ar-C), 128.59 (C_{quat}, Ar-C), 139.99 (C_{quat}, C-1); MS (70 eV): *m*/*z* (%): 243 (12) [M^+], 228 (5) [$M^+ - CH_3$], 198 (1) [$M^+ - C_2H_4O$], 156 (1) [M^+ – morpholine – H], 128 (6) [M^+ – morpholine – C_2H_4], 114 (100) [$M^+ - C_6H_5 - C_4H_4$]; elemental analysis calcd for (%) $C_{16}H_{21}NO$ (243.4) calcd: C 78.97, H 8.70, N 5.76; found: C 79.20, H 8.69, N 5.92.

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Insertion Reactions of Nitriles into the P–C Bond of $[(\eta^1\text{-}C_5Me_5)P\{W(CO)_5\}_2]$—A Novel Approach to Phosphorus-Containing Heterocycles**

Michael Schiffer and Manfred Scheer*

Dedicated to Professor Dieter Sellmann in occasion of his 60th birthday

In the thermal activation of $[Cp^*P\{W(CO)_5\}_2]$ (**1**; $Cp^* = \eta^1\text{-}C_5Me_5$), a Cp* migration from the P atom to the transition metal atom occurs to form the highly reactive intermediate $[Cp^*(CO)_2W{\equiv}P \rightarrow W(CO)_5]$ **A**.[1] The chemistry of this highly reactive intermediate **A** offers promising synthetic routes to a large variety of new phosphametallaheterocycles. Thus, the trapping reaction of **A** with phosphaalkynes[1] and alkynes[2] proceeds by formal [2+2] cycloaddition reactions to form novel main group element transition metal cage compounds. In continuation of these reactivity studies we attempted to employ nitriles for trapping reactions of intermediate **A**. Surprisingly, however, we observed insertion reactions into the P–C bond of the starting material.

Insertion reactions of organonitriles into metal–hydrogen and metal–carbon bonds are established processes.[3] Furthermore, it is known that nitriles insert into the Mo–Cl bond of $MoCl_5$,[4] into the Zr–O bond of $[Cp^*_2Zr{=}O]$,[5] and into E–N bonds (E = B,[6] Al,[7] P,[8] Pt[9]). Recently, Neumüller et al. reported on CsX-catalyzed trimerization reactions of acetonitrile with EMe_3 (E = element of Group 13) under elimination of CH_4 and formation of $[Me_2E\{HNC(Me)\}_2$-

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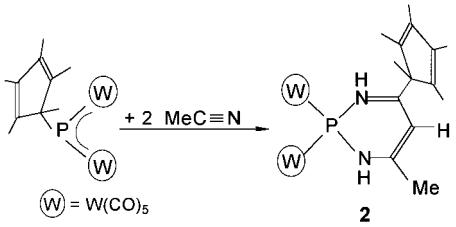
CCN] (E = Al,[10] Ga,[11] In[12]). However, in contrast, nitriles insert into a P–C bond only in the case of strained three-membered rings of the 2*H*-azaphosphirene at higher temperatures as has been shown only recently by Streubel et al.[13]

We report herein on a smooth insertion of nitriles into the unstrained P–C bond of [Cp*P{W(CO)$_5$}$_2$] (**1**), which already proceeds at ambient temperatures to give dihydro-1,3,2-diazaphosphinine and benzo-1,2-azaphosphole derivatives. The synthesis of the latter compound is accompanied by an additional C–H bond activation at room temperature and offers a novel and straightforward synthetic approach to this class of compounds.

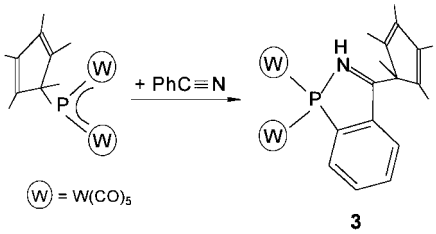
Stirring the dark blue solution of **1** in toluene with an excess of acetonitrile [Eq. (1)] results in a color change to red at room temperature.[14] After workup and crystallization from



(1)

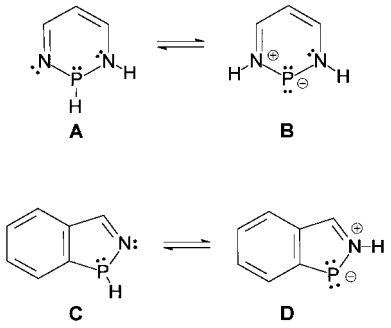
dichloromethane, the 1,2-dihydro-1,3,2-diazaphosphinine derivative **2** was obtained as red crystals in 88 % yield. Complex **2** shows that two acetonitrile molecules have been inserted into the P–C bond of **1**, under C–C bond formation and subsequent migration of the β-H atoms of one acetonitrile to the N atoms. Thereby one molecule of acetonitrile loses two hydrogen atoms of its methyl group. To check this hypothesis of the 1,3-H shift of acetonitrile to the N atoms, reaction (1) was carried out with CD_3CN. Indeed, the obtained product **2a** contains deuterium at the N atoms, which confirms the 1,3-D shift.

To avoid the observed insertion reaction and to obtain a [2+2] cycloaddition product from the intermediate [Cp*(CO)$_2$W≡P→W(CO)$_5$] **A** and the C≡N triple bond of a nitrile, we used exclusively organonitriles without β-hydrogen atoms. However, when *t*BuC≡N was used as the trapping reagent in the thermolysis reaction, it was found not to react with **1**. No product, even an insertion or addition product, could be detected by ^{31}P{^{1}H} NMR spectroscopy even after refluxing in toluene for 48 h. However, the use of benzonitrile in the reaction with **1** at ambient temperature[14] leads to a dark red toluene solution which affords after workup dark red crystals of 3,4-benzo-1*H*-1,2-azaphosphole **3** in 43 % yield [Eq. (2)]. The formation of the **3** indicates that after insertion of the nitrile into the P–C bond, a C–H bond activation occurs.



(2)

The synthesis of 1,3,2-diazaphosphinines[15] and benzo-1,2-azaphospholes[16] is so far restricted to the use of dimethyltitanocene and diphenylzirconocene complexes. Thus, our approach appears to provide an alternative synthesis for such derivatives. Furthermore, it should be mentioned that alkylation of benzo-2*H*-1,2-azaphospholes was observed at the P atom of the heterocycle[16] and 1,3,2-diazaphosphinines react readily at room temperature with protic reagents to give 1,2-dihydro-1,3,2-diazaphosphinines.[15] Complexes **2** and **3** are in principle the betaine-type tautomers **B** and **D** of 1,2-dihydro-1,3,2-diazaphosphinine **A** and benzo-2*H*-1,2-azaphosphole **C**, respectively, stabilized by [W(CO)$_5$] moieties at the P atoms.



Compounds **2** and **3** are red crystalline solids, readily soluble in hexane, toluene, and CH_2Cl_2 and are stable in air for a short period of time. The IR spectra of both compounds display CO stretching frequencies for terminal CO ligands. The mass spectra of **2** and **3** show the molecular ion peaks as well as additional fragments revealing the subsequent loss of CO.

The ^{31}P NMR spectrum of **2** reveals a pseudotriplet (doublet of doublets) at $\delta = 176.2$ with one pair of ^{183}W satellites, which are also split into pseudotriplets due to the coupling of the phosphorus atom to the two almost identical hydrogen atoms bound to the nitrogen atoms (^2J(P,H) = 22 Hz). The coupling constant ^1J(W,P) of 202 Hz is comparable to those of other terminally bound [W(CO)$_5$] groups.[17] For **2** the existence of a methine proton at the C(13) atom is confirmed by its ^{1}H NMR spectrum as well as by a ^{13}C{DEPT} spectrum. Furthermore, for the D-containing complex [Cp*CC(D)C(CD$_3$)N(D)P{W(CO)$_5$}$_2$N(D)] **2a**, the ^{31}P NMR spectrum reveals only one singlet at $\delta = 175.2$ with a ^1J(W,P) coupling of 201 Hz and the ^{1}H NMR spectrum shows only the protons of the Cp* group. The ^{31}P{^{1}H} NMR spectrum of **3** reveals a singlet at $\delta = 90.6$ with a ^1J(W,P) coupling of 162 Hz. The coupling of the P atom to the NH proton could not be resolved, even in the ^{1}H NMR spectrum.

The X-ray crystal structure analysis of **2**[18] (Figure 1) reveals the six-membered ring of a 1,2-dihydro-1,3,2-diazaphosphinine derivative. Thus, the tetrahedrally coordinated phosphorus atom is bent by 29.6 (2)° out of the plane of the remaining ring formed by the atoms N(1), C(11), C(13), C(14), and N(2). The phosphorus atom is further connected to two [W(CO)$_5$] moieties. In comparison to the W–P bond lengths in the starting phosphinidene complex **1** (2.445(2), 2.428(2) Å), which are indicative of multiple-bond character, the W–P bond lengths in **2** (2.5409(12), 2.5311(14) Å) are

  1433-7851/01/4018-3414 $ 17.50+.50/0 *Angew. Chem. Int. Ed.* **2001**, *40*, No. 18

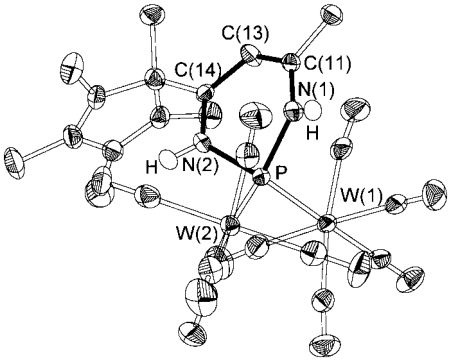


Figure 1. Molecular structure of **2** in the crystal; thermal ellipsoids are drawn at the 30% probability level (hydrogen atoms (except the NH protons) are omitted for clarity); selected bond lengths [Å] and angles [°]: W(1)-P 2.5409(12), W(2)-P 2.5311(14), P-N(1) 1.763(4), P-N(2) 1.765(4), N(1)-C(11) 1.331(6), N(2)-C(14) 1.342(6), C(11)-C(12) 1.495(6), C(11)-C(13) 1.396(7), C(13)-C(14) 1.392(6); N(1)-P-N(2) 92.48(18), N(1)-P-W(2) 107.37(14), N(2)-P-W(2) 111.07(14), N(1)-P-W(1) 107.26(13), N(2)-P-W(1) 111.06(14), W(2)-P-W(1) 123.04(5), C(11)-N(1)-P 126.1(3), C(14)-N(2)-P 125.2(3), N(1)-C(11)-C(13) 121.4(4), N(1)-C(11)-C(12) 118.5(4), C(14)-C(13)-C(11) 121.1(4), N(2)-C(14)-C(13) 121.4(4).

significantly longer. The slightly longer P–N single bond lengths in **2** are almost identical (1.763(4), 1.765(4) Å) and are in good agreement with the apical P–N single bond length in 5,6-benzo-1,3-dimethyl-2-dimethylamino-8,8,9,9-tetrakis(trifluoromethyl)-1,3-diaza-7,10-dioxa-2-λ^5-phosphaspiro[4,5]decan-4-one (1.767(2) Å).[19] All other N–C and C–C bond lengths of the six-membered ring of **2** are in good agreement with those of cyclic conjugated ring systems.[20]

The X-ray crystal structure analysis of **3** (Figure 2)[18] reveals a planar benzo-1*H*-1,2-azaphosphole derivative, in which the phosphorus atom is coordinated by two $[W(CO)_5]$ moieties in a distorted tetrahedral geometry. The W(1)–P (2.5494(17) Å) and W(2)–P bond lengths (2.5396(18) Å) are comparable to the W–P bond lengths in complex **2**. The P–N (1.775(5) Å) bond length corresponds to a P–N single bond, whereas the N–C(11) bond length (1.311(7) Å) corresponds to a N–C double bond. All other C–C distances are in good agreement with those of cyclic conjugated benzo-1,2-azaphosphole systems.

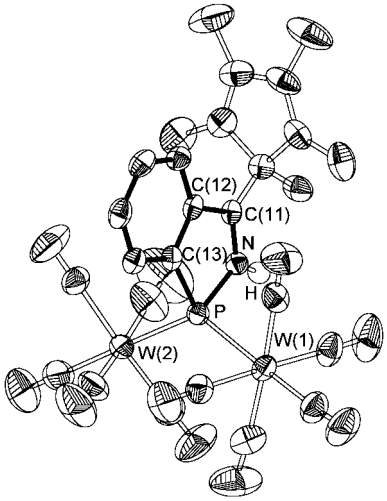


Figure 2. Molecular structure of **3** in the crystal; thermal ellipsoids are drawn at the 30% probability level (hydrogen atoms (except the NH protons) are omitted for clarity); selected bond lengths [Å] and angles [°]: W(1)-P 2.5494(17), W(2)-P 2.5396(18), P-N 1.775(5), P-C(13) 1.802(6), N-C(11) 1.311(7), C(11)-C(12) 1.467(7), C(12)-C(13) 1.398(8), C(13)-C(14) 1.400(8), C(14)-C(15) 1.375(9), C(15)-C(16) 1.379(10), C(16)-C(17) 1.373(8), C(12)-C(17) 1.415(8); N-P-C(13) 86.4(2), N-P-W(2) 107.68(17), C(13)-P-W(2) 108.63(19), N-P-W(1) 108.39(16), C(13)-P-W(1) 107.05(19), W(2)-P-W(1) 130.02(6), C(11)-N-P 118.3(4), N-C(11)-C(12) 110.7(5), C(13)-C(12)-C(11) 111.7(5), C(12)-C(13)-P 112.9(4), C(14)-C(13)-C(11) 121.1(4), N(2)-C(14)-C(13) 121.4(4).

To shed light onto the pathway of the insertion, we carried out reaction (1) with the starting materials in a 1:1 ratio at room temperature. Even after 48 h, there was no change of color, and no additional signal was observed in the ^{31}P NMR spectrum. Titration of the solution with additional CH_3CN to a **1**:CH_3CN ratio of 1:1.4 led to color change, which was accompanied by the appearance of an additional signal at $\delta =$ 119.3 in the ^{31}P NMR spectrum. Unfortunately it was not possible to isolate any compound from this solution. This signal disappears when the color of the solution turns to red at a **1**:CH_3CN ratio of 1:5. For the transient ^{31}P NMR signal, we propose the formation of an adduct of the formula $[Cp^*P\{W(CO)_5\}_2(NCMe)]$, since it is known that phosphinidene complexes $[RP\{W(CO)_5\}_2]$ behave as Lewis acids. Owing to the electron deficiency at the phosphorus atom, Lewis bases can add at the central P atom leading to complexes with a tetrahedrally coordinated phosphorus atom.[21] Such initially formed compounds seem to be plausible for reactions (1) and (2), a subsequent insertion reaction into the P–C σ-bond gives the formed products. While for reaction (2) a C–H bond activation occurs to form the benzo-1*H*-1,2-azaphosphole derivative, for reaction (1) presumably a second molecule of acetonitrile is subsequently added followed by a cyclization reaction under migration of two protons of the methyl group of the Cp*-substituted MeCN unit.

The reported insertion of nitriles into the C–P bond of the phosphinidene complex **1** is a novel reaction pattern for this compound. Besides the formation of the intermediate $[Cp^*(CO)_2W{\equiv}P{\rightarrow}W(CO)_5]$ **A** containing a W–P triple bond,[1, 2] and a Cp* elimination,[22] also an insertion reaction into the unstrained P–C σ bond of **1** proceeds under very mild conditions. With benzonitrile as a reaction component an additional C–H bond activation occurs. The described reaction provides a straightforward route for the synthesis of novel phosphorus heterocycles.

Experimental Section

2: Me–C≡N (0.780 g, 0.019 mol) was added to a solution of **1**[23] (0.630 g, 0.77 mmol) in toluene (40 mL) and stirred for two hours at room temperature (or refluxed for one hour). The solvent was completely removed in vacuo and the resulting residue was dissolved in dichloromethane (5 mL). Red crystals of **2** (0.609 g, 0.68 mmol, 88%) were obtained at −25 °C. $^{31}P\{^1H\}$ NMR (101.256 MHz, [D_6]benzene, 298 K, 85% H_3PO_4 ext.): $\delta = 176.2$ (t, $^1J(P,H) = 22$, $^1J(W,P) = 202$ Hz); ^1H NMR (250.113 MHz, [D_6]benzene, 298 K, TMS): $\delta = 4.88$ (br, 1H; NH), 4.26 (br, 1H; NH), 1.58 (s, 6H; CH_3(Cp*)), 1.51 (s, 6H; CH_3(Cp*)), 0.98 (s, 3H; CH_3), 0.84 (s, 3H; CH_3), 0.31 (s, 1H; CH); IR (KBr): $\tilde{\nu} = 2075$ (s), 2050 (s), 1990 (sh), 1920 (br) (4 × ν(CO)), 1544 cm^{-1} (w) (δ(NH)); MS (EI): *m*/*z* (%): 896 (27) [M^+], 868 (17) [$M^+ - CO$], 812 (28) [$M^+ - 3CO$], 728 (26) [$M^+ - 6CO$], 672 (29) [$M^+ - 8CO$], 616 (100) [$M^+ - 10CO$], 571 (25) [$M^+ - (CO)_{10}(CH_3)_3$]; elemental analysis (%) calcd for $C_{24}H_{21}N_2O_{10}PW_2$ (896.11): C 32.17, H 2.36, N 3.13; found: C 31.86, H 3.01, N 2.81.

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2a: The corresponding reaction of **1** (0.104 g, 0.13 mmol) with $CD_3C{\equiv}N$ (1.0 mmol) in toluene (40 mL) at room temperature led after stirring for 2 h to a red solution of **2a**. After complete removal of the solvent, the residue was recrystallized from dichloromethane to give **2a** (0.100 g, 0.11 mmol, 85%) at $-25\,^{\circ}C$. $^{31}P\{^1H\}$ NMR (101.256 MHz, [D_6]benzene, 298 K, 85% H_3PO_4 ext.): $\delta = 175.2$ (s, $^1J(W,P) = 201$ Hz); ^1H NMR (250.113 MHz, [D_6]benzene, 298 K, TMS): $\delta = 1.58$ (s, 6H; CH_3(Cp*)), 1.51 (s, 6H; CH_3(Cp*)), 0.98 (s, 3H; CH_3(Cp*)).

3: PhC≡N (0.028 g, 0.27 mmol) was added to a solution of **1** (0.20 g, 0.25 mmol) in toluene (40 mL) and stirred for 2 h at room temperature (or refluxed for one hour). The solvent of the orange-colored solution was completely removed in vacuo and the resulting residue was extracted with *n*-pentane to give red crystals of **3** (0.099 g, 0.108 mmol, 43%) at $-25\,^{\circ}C$. $^{31}P\{^1H\}$ NMR (101.256 MHz, [D_6]benzene, 298 K, 85% H_3PO_4 ext.): $\delta =$ 90.6 (s, $^1J(W,P) = 162$ Hz); ^1H NMR (250.113 MHz, [D_6]benzene, 298 K, TMS): $\delta = 7.92 - 6.65$ (aromatic protons), 3.55 (s, 1H; NH), 1.50 (s, 6H; CH_3(Cp*)), 1.48 (s, 6H; CH_3(Cp*)), 1.15 (s, 3H; CH_3(Cp*)); IR (KBr): $\tilde{\nu} =$ 1985 (w), 1980 (w), 1965 (sh), 1910 cm^{-1} (br) ($4 \times \nu$(CO)); MS (EI): *m*/*z* (%): 917 (6) [M^+], 889 (10) [$M^+ - CO$], 861 (10) [$M^+ - 2CO$]; elemental analysis (%) calcd for $C_{27}H_{20}NO_{10}PW_2$ (917.13): C 35.36, H 2.20, N 1.53; found: C 35.39, H 2.29, N 1.58.

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[18] Crystal structure analyses of **2** and **3** were performed on a STOE IPDS diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods with the program SHELXS-93,[24a] and full-matrix least-squares refinement on F^2 in SHELXL-97[24b] was performed with anisotropic displacements for non-H atoms. Hydrogen atoms were located in idealized positions and refined isotropically according to the riding model. **2**: $C_{24}H_{21}N_2O_{10}PW_2$, $M_r = 896.10$, crystal dimensions $0.15 \times 0.15 \times 0.04$ mm^3, monoclinic, space group $P2_1/n$ (no. 14); $a = 10.753(2)$, $b = 11.986(2)$, $c = 22.052(4)$ Å, $\beta = 94.65(3)^{\circ}$, $T = 200(1)$ K, $Z = 4$, $V = 2832.8(10)$ $Å^3$, $\rho_{calcd} = 2.101$ $Mg\,m^{-3}$, $\mu(Mo_{K\alpha}) = 8.227$ mm^{-1}, 5448 independent reflections ($R_{int} = 0.0572$, $2\theta_{max} = 52^{\circ}$), 4449 observed with $F_o = 4\sigma(F_o)$; 358 parameters, $R_1 = 0.0316$, $wR_2 = 0.0798$. **3**: $C_{15}H_{20}NO_{10}PW_2$, $M_r = 917.11$, crystal dimensions $0.20 \times 0.12 \times 0.10$ mm^3, monoclinic, space group $P2_1/c$ (no. 14); $a = 15.643(3)$, $b = 15.738(3)$, $c = 13.126(3)$ Å, $\beta = 110.86(3)^{\circ}$, $T = 253(1)$ K, $Z = 4$, $V = 3019.5(10)$ $Å^3$, $\rho_{calcd} = 2.017$ $Mg\,m^{-3}$, $\mu(Mo_{K\alpha}) = 7.720$ mm^{-1}, 5799 independent reflections ($R_{int} = 0.0579$, $2\theta_{max} = 52^{\circ}$), 4751 observed with $F_o = 4\sigma(F_o)$; 375 parameters, $R_1 = 0.0356$, $wR_2 = 0.0914$. 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-161080 (**2**) and CCDC-161081 (**3**). 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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