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An Unprecedented κ^3-[N,C,N] Coordination Mode of the Bis(3,4,5-trimethylpyrazol-1-yl)methide Ligand

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Summary: Treatment of triarylstannyl-bis(3,4,5-trimethylpyrazol-1-yl)methane, $Ar_3SnCH(3,4,5-Me_3Pz)_2$ (Ar = phenyl or p-tolyl), with $W(CO)_5THF$ results in the oxidative addition of the tin−carbon(sp^3) bond to the tungsten(0) center to yield the heterodinuclear complexes $CH(3,4,5-Me_3Pz)_2(CO)_3W{-}SnAr_3$, in which four-membered metallacycles are found and bis(3,4,5-trimethylpyrazol-1-yl)methide acts as a tridentate monoanionic κ^3-[N,C,N] chelating ligand.

Poly(pyrazol-1-yl)alkanes were first reported to form transition-metal complexes by Trofimenko in 1970.[1] After that, and especially after an improved synthetic method was developed by Julia et al.,[2] the coordination chemistry of these ligands has received increasing attention.[3,4] A number of main-group[5] and transition-metal[6] complexes containing poly(pyrazol-1-yl)alkanes have been synthesized and characterized in recent years. To advance the development of poly(pyrazol-1-yl)alkane chemistry, some new higher yield and higher purity synthetic methods for poly(pyrazol-1-yl)alkanes have been explored.[5b,7] In recent years, modification of the central carbon atom by the organic functional groups to form heteroscorpionate ligands has also been successful. These new heteroscorpionate ligands usually have asymmetric N_2O,[8] N_2S,[9] or N_3O[10] coordination environments. Recently, replacement of the central carbon atom by the silicon atom to form poly(pyrazol-

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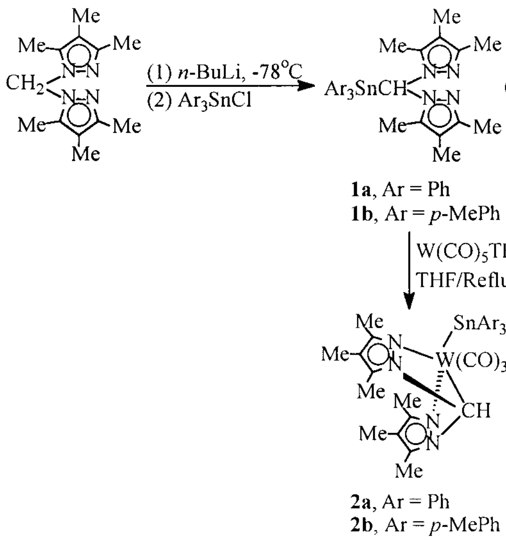
1-yl)silanes has been reported.[11] However, the modification of poly(pyrazol-1-yl)alkanes by substitution of organometallic groups on the central carbon atom is rare.[12] Such poly(pyrazol-1-yl)alkanes are expected to have unusual reactivity, owing to the introduction of the organometallic groups. In this paper we report the synthesis of two new poly(pyrazol-1-yl)alkanes modified by introduction of organotin groups on the central carbon atom and their reaction with $W(CO)_5THF$ to yield heterodinuclear complexes containing four-membered metallacycles, in which bis(3,4,5-trimethylpyrazol-1-yl)methide acts as an unprecedented tridentate monoanionic κ^3-[N,C,N] chelating ligand.

The modification of bis(3,4,5-trimethylpyrazol-1-yl)methane by substitution of organotin groups on the central carbon atom was readily carried out by reaction of (bis(3,4,5-trimethylpyrazol-1-yl)methyl)lithium[13] with a triaryltin chloride as shown in eq 1. Treatment of **1a** and **1b** with $W(CO)_5THF$ in refluxing THF resulted in the oxidative addition of the $Sn-C_{sp^3}$ bond to the tungsten(0) center to yield the novel four-membered metallacyclic complexes **2**,[14] which were characterized by ^1H NMR spectroscopy, their IR spectra, and elemental analyses, as well as X-ray structure analyses of **2a** and **2b**.



(1)

Complexes **2** are air-stable in the solid state, and even their solutions could be manipulated in air. The proton signal of the CH group in **1** is remarkably different from that in **2**, which appears at 6.50 ppm for **1a** and 6.70 ppm for **1b**, respectively, but is considerably shifted to higher field in **2**, appearing at 4.34 ppm for **2a** and **2b**. The smaller electronegativity of tungsten compared with that of tin may be responsible for this upfield shift. Three strong ν(CO) bands in the range 1970−1840 cm^{-1} are observed in the IR spectrum of **2**, which is consistent with the tricarbonyltungsten species.

The structures of **2** have also been confirmed by X-ray crystallography.[15] The crystal structure of **2a** (Figure 1) is similar to that of **2b** (Figure 2, in the Supporting Information). They clearly show that the triarylstannyl groups have been transferred to the tungsten center and that new tungsten−saturated carbon and tungsten−tin bonds have been formed. The seven-coordinate tungsten atom in **2a** or **2b** is best described as a capped octahedron with the triarylstannyl groups in the capping position. The capped face is made up of C(1), C(2), and C(4) atoms for **2a** and C(1), C(2), and C(10) atoms for **2b**. The W−Sn distance is 2.7795(4) Å in **2a** and 2.7845(15) Å in **2b**, which is within the normal range for W−Sn bonds.[16] The most interesting structural feature of **2** is that bis(3,4,5-trimethylpyrazol-1-yl)methide acts as a tridentate, monoanionic κ^3-[N,C,N] chelating ligand, resulting in formation of two novel four-membered metallaheterocycles. This coordination mode has not been reported previously for poly(pyrazol-1-yl)alkane

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(13) To a solution of bis(3,4,5-trimethylpyrazol-1-yl)methane (2 mmol) in THF (40 mL) under Ar was added a hexane solution of *n*-BuLi (2 M, 1.0 mL) at −78 °C, and the mixture was stirred for 1 h at that temperature. To the mixture was added a solution of the triaryltin chloride (2 mmol) in THF (10 mL). The reaction mixture was stirred at −78 °C for 1 h, allowed to slowly reach room temperature, and stirred overnight. The solvent was removed under reduced pressure, and the residual solid was recrystallized from hexane to yield white crystals. Physical and spectroscopic data for **1a** are as follows. Yield: 49%. Mp: 132−134 °C. Anal. Found: C, 64.05; H, 5.88; N, 9.57. Calcd for $C_{31}H_{34}N_4Sn$: C, 64.03; H, 5.85; N, 9.64. IR (KBr, cm^{-1}): 1577.7 s (ν(pyrazole ring)). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.77, 1.80, 2.11 (s, s, s, 6H, 6H, 6H, CH_3), 6.50 (s, 1H, CH), 7.38−7.65 (m, 15H, C_6H_5). Physical and spectroscopic data for **1b** are as follows. Yield: 51%. Mp: 150−152 °C. Anal. Found: C, 65.40; H, 6.38; N, 9.01. Calcd for $C_{34}H_{40}N_4Sn$: C, 65.49; H, 6.42; N, 8.99. IR (KBr, cm^{-1}): 1584.3 s (ν(pyrazole ring)). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.76, 2.12 (s, s, 12H, 6H, CH_3), 2.30 (s, 9H, *p*-$CH_3C_6H_4$), 6.70 (s, 1H, CH), 7.23, 7.43 (d, d, 6H, 6H, *p*-$CH_3C_6H_4$).

(14) Compounds **1** (0.3 mmol) were added to a solution of $W(CO)_5THF$ in THF, prepared in situ by the irradiation of a solution of $W(CO)_6$ (0.3 mmol) in THF (20 mL) for 8 h, and the mixture was stirred and heated at reflux for 2 h. After the reaction was complete, the solvent was removed under reduced pressure, and the residual solid was purified by column chromatography on alumina using CH_2Cl_2/hexane (1/2 v/v) as eluent. The eluate was concentrated to dryness under reduced pressure, and the residual solid was recrystallized from CH_2Cl_2/hexane to give orange-red crystals. Spectroscopic data for **2a** are as follows. Yield: 41%. Anal. Found: C, 47.10; H, 3.59; N, 6.30. Calcd for $C_{34}H_{34}N_4O_3SnW\cdot 0.25CH_2Cl_2$: C, 47.23; H, 3.96; N, 6.43. IR (KBr, cm^{-1}): 1970.0 s, 1876.0 s, 1843.0 s (ν(CO)). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.73, 1.83, 2.24 (s, s, s, 6H, 6H, 6H, CH_3), 4.34 (s, 1H, CH), 5.29 (s, 0.5H, CH_2Cl_2), 7.23−7.44 (m, 15H, C_6H_5). Spectroscopic data for **2b** are as follows. Yield: 33%. Anal. Found: C, 46.46; H, 4.27; N, 5.92. Calcd for $C_{37}H_{40}N_4O_3SnW\cdot CH_2Cl_2$: C, 46.71; H, 4.30; N, 5.74. IR (KBr, cm^{-1}): 1969.9 s, 1878.3 s, 1839.7 s (ν(CO)). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.73, 1.82, 2.22 (s, s, s, 6H, 6H, 6H, CH_3), 2.27 (s, 9H, *p*-$CH_3C_6H_4$), 4.34 (s, 1H, CH), 5.28 (s, 2H, CH_2Cl_2), 7.03, 7.23 (d, d, 6H, 6H, *p*-$CH_3C_6H_4$).

(15) Crystallographic data for **2a**: triclinic, $P\bar{1}$, $a = 9.6379(7)$ Å, $b = 13.684(1)$ Å, $c = 13.876(1)$ Å, $\alpha = 97.379(1)°$, $\beta = 94.724(1)°$, $\gamma = 94.196(1)°$, $V = 1802.2(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.604$ g cm^{-3}, $T = 298$ K, 6326 unique reflections, 5623 with $I > 2\sigma(I)$, R (R_w) = 0.0294 (0.0848). Crystallographic data for **2b**: monoclinic, $P2_1/n$, $a = 10.541(5)$ Å, $b = 22.32(1)$ Å, $c = 17.059(9)$ Å, $\beta = 93.928(9)°$, $V = 4004(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.619$ g cm^{-3}, $T = 293$ K, 16 397 collected reflections, 7005 with $I > 2\sigma(I)$, R (R_w) = 0.0436 (0.0791).

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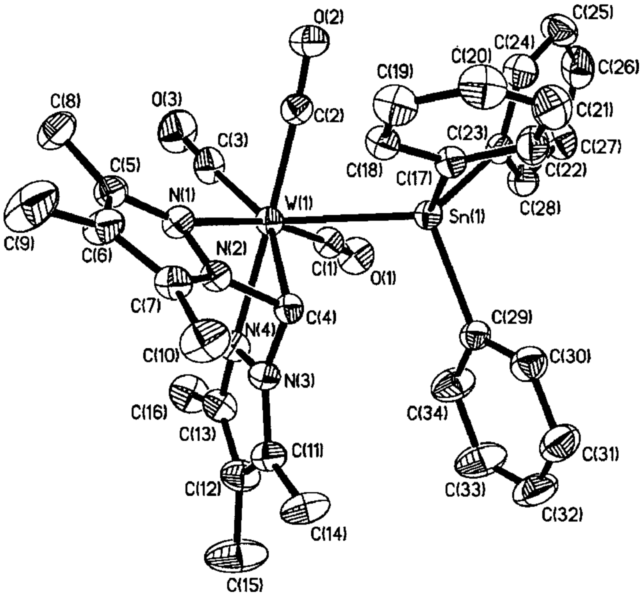

Figure 1. Molecular structure of **2a**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): W(1)−N(1) = 2.222(4), W(1)−N(4) = 2.243(4), W(1)−C(4) = 2.326(5), W(1)−Sn(1) = 2.7795(4), N(3)−C(4) = 1.462(6), N(2)−C(4) = 1.458(6); N(1)−W(1)−N(4) = 82.00(16), C(3)−W(1)−C(4) = 155.6(2), N(1)−W(1)−C(4) = 60.63(16), N(4)−W(1)−C(4) = 60.51(15), N(2)−C(4)−N(3) = 109.2(4), N(2)−C(4)−W(1) = 91.1(3), N(3)−C(4)−W(1) = 91.2(3).

ligands. It is also noteworthy that in the four-membered metallaheterocycles the angles ∠N−C−W are very close to 90°.

The oxidative addition of a tin−phenyl carbon bond to a tungsten(0) center to yield W−Sn bonded complexes with a κ^3-[C,N,N′] ligand has been reported,[17] but there is no prior report of tungsten complexes containing sp^3-hybridized carbon in κ^3-[N,C,N] ligands.[18] The present report also exhibits a novel coordination mode for poly(pyrazol-1-yl)alkanes. The other interesting aspect of the present report is that stable metallacyclic complexes having an M−M′ bond can be formed under mild conditions. In view of known catalytic processes involving the formation of metallacyclic fragments, and the potential catalytic activity of heterobimetallic complexes, the present results are of some interest. Furthermore, the present results suggest that poly(pyrazol-1-yl)alkanes with organometallic groups on the central carbon may have distinctive reactivity, and modification of the central carbon using a more extensive range of organometallic groups is in progress.

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Supporting Information Available: Tables of crystallographic data, atom coordinates, thermal parameters, and bond distances and angles for **2a** and **2b** and an ORTEP plot of **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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