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Hydrotris(pyrazolyl)borate Metallacycles: Conversion of a Late-Metal Metallacyclopentene to a Stable Metallacyclopentadiene−Alkene Complex

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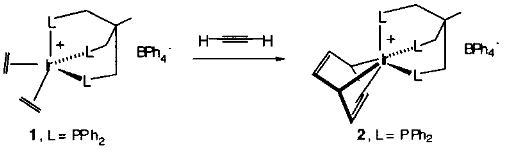
The role of late-metal metallacyclopentenes and metallacyclopentadienes in the metal-mediated reactions of alkynes has directed attention toward the chemistry of iridium metallacycles containing phosphine ancillary ligands.[1,2] Motivated by recent advances in the organometallic chemistry of trispyrazolylborate iridium complexes,[3] we set out to develop synthetic routes toward metallacyclopentadiene complexes bearing the hydrotris(pyrazolyl)borate (Tp) ancillary ligand. Here we report preliminary results in this area, including (1) the first structurally characterized iridacyclopent-2-ene complex, (2) the first example of a hydrotris(pyrazolyl)borate metallacyclopentadiene complex, one that is formed by the unprecedented conversion of a late-metal metallacyclopentene to a metallacyclopentadiene complex, and (3) the first example of a stable metallacyclopentadiene−alkene complex.

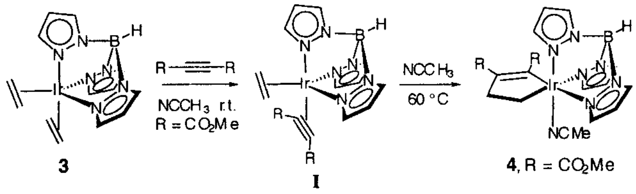
Bianchini's observation that the iridium bis(ethylene) complex $[\{MeC(CH_2PPh_2)_3\}Ir(CH_2{=}CH_2)_2]BPh_4$ (**1**) undergoes reaction with ethyne at room temperature to give the η^4-benzene complex **2** (Scheme 1)[4] suggested that $[(Tp)Ir(C_2H_4)_2]$ (**3**)[5] may serve as an appropriate precursor to trispyrazolylborate−metallacyclopentadienes. Iridium(III) Tp−metallacycles are expected to be significantly more electron rich than cationic triphos analogues, based on the IR spectroscopic data (ν_{CO}) for $[(Tp)Ir(CO)(H)_2]$ (2020 cm^{-1}) and $[\{MeC(CH_2PPh_2)_3\}Ir(CO)(H)_2]PF_6$ (2085 cm^{-1}).[6]

Carmona previously demonstrated that heating **3** in acetonitrile at 60 °C led to formation of the vinyl−alkyl iridium(III) complex $[(Tp)Ir(CH_2CH_3)(CH{=}CH_2)(NCMe)]$, which upon further heating in acetonitrile (100 °C) underwent coupling of the nitirile and vinyl ligand to form an iridapyrrole complex, $[(Tp)Ir\{CH{=}CHCMe{=}NH\}(CH_2CH_3)]$.[7] We now report that heating an acetonitrile (20 mL) solution of **3** (0.20) in the presence of dimethyl acetylenedicarboxylate (DMAD, 0.30 mmol) at 60 °C (30 min) leads to the isolation of an off-white solid, identified as the metallacyclopent-2-ene complex $[(Tp)Ir\{CH_2CH_2C(CO_2Me){=}C(CO_2Me)\}(NCMe)]$ (**4**, 95% yield; Scheme 2).[8] In addition to signals assigned to the Tp hydrogens, a ^1H NMR spectrum ($CDCl_3$) of **4** exhibited resonances which were consistent with a structure that incorporated ethene [δ 2.97 (m, 2H), 2.43 (m, 1H), and 2.25 (m, 1H)], DMAD [3.68 (3H), 3.36 (3H)], and acetonitrile [2.48 (3H)]. In the ^{13}C NMR ($CDCl_3$) spectrum of **4**, signals at −0.8 and 36.9 ppm were assigned to the Ir*C*H_2 and $IrCH_2$*C*H_2 carbons of the metallacyclopent-2-ene. For comparison, the metallabenzocyclopentene $[(Tp)Ir(CH_2CH_2\text{-}o\text{-}C_6H_4)(CH_2{=}CH_2)]$ exhibits ^{13}C NMR (C_6D_6) resonances at −4.4 (Ir*C*H_2) and 40.8 ($IrCH_2$*C*H_2) ppm.[9,10]

Scheme 1



Scheme 2



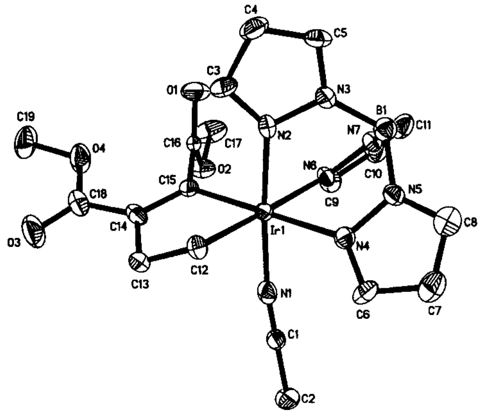


Figure 1. ORTEP diagram (50% thermal ellipsoid probabilities) for **4**. Selected bond lengths (Å) and angles (deg): Ir−N(1) 1.990(6), Ir−N(2) 2.031(6), Ir−N(4) 2.122(5), Ir−N(6) 2.163(5), Ir−C(12) 2.066(6), Ir−C(15) 2.042(6), C(12)−C(13) 1.520(9), C(13)−C(14) 1.517(9), C(14)−C(15) 1.358(9), C(15)−C(16) 1.485(9); N(2)−Ir−C(15) 90.6(2), N(2)−Ir−C(12) 92.4(2), C(15)−Ir−N(4) 175.1(2), C(15)−Ir−N(6) 98.9(2), N(4)−Ir−N(6) 85.2(2), C(15)−Ir−C(12) 79.4(3), C(12)−C(13)−C(14) 107.7(5), C(15)−C(14)−C(13) 115.1(6), Ir−C(12)−C(13) 110.1(4), Ir−C(15)−C(14) 116.7(5).

The structure of **4** was confirmed by X-ray crystallography (Figure 1).[11] The metallacyclopentene ring in **4** exhibits a pronounced 34.6° fold angle between the Ir−C(12)−C(13) and Ir−C(13)−C(14)−C(15) mean planes. The metallacycle carbons C(13) and C(14) deviate from the mean plane defined by Ir−C(12)−C(15)−N(4)−N(6) by −0.65 and −0.28 Å, respectively. The iridium−nitrogen bond trans to the sp^3 ring carbon is 0.04 Å longer than the iridium−nitrogen bond trans to the sp^2 ring hydrogen.

The formation of **4** from **3** presumably involves substitution of one alkene ligand by DMAD to generate an η^2-alkene/η^2-alkyne intermediate (**I**, Scheme 2). A small-scale reaction of **3** (0.011 mmol) and DMAD (0.023 mmol) was therefore carried out at room temperature in CD_3CN (0.52 mL). A ^1H NMR spectrum of the solution indicated quantitative conversion of **3** to a new compound that exhibited broad singlets at δ 8.01, 7.81, and 6.31 (Tp hydrogens), as well as singlets at 3.74 (6 H) and 3.45 (4H) consistent with both η^2-DMAD and η^2-C_2H_4 ligands. A reasonable structure for this complex is the fluxional η^2-alkene/η^2-alkyne

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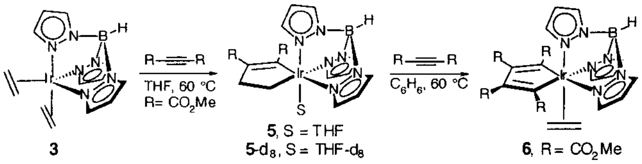
Scheme 3



complex **I**, although a fluxional κ^2-Tp complex containing a $NCCD_3$ ligand cannot be ruled out.

Iridacyclopentene **4** failed to undergo reaction with either phenylacetylene or carbon monoxide in benzene-d_6, even at temperatures up to 100 °C (18 h); while heating **4** in acetonitrile-d_3 at 100 °C for 21 h gave less than 5% of **4**-d_3. In an effort to prepare analogues of **4** with a more labile axial ligand, the reaction of **3** (0.2 mmol) with DMAD (0.3 mmol) was carried out in THF (15 mL) solvent. After heating at 60 °C for 30 min, the THF adduct $[(Tp)Ir\{CH_2CH_2C(CO_2Me){=}C(CO_2Me)\}(THF)]$ (**5**) was isolated as an impure yellow solid in ca. 67% yield (Scheme 3). Attempts to purify **5** by recrystallization resulted in decomposition. The assigned structure for **5** is therefore based on the ^1H NMR spectrum in THF-d_8, which exhibited DMAD hydrogen singlets [δ 3.5 (s, 3H), 3.2 (s, 3H)] and ethene hydrogen multiplets [3.2 (2H), 3.0 (1H), and 2.4 (1H)] of similar chemical shift as those observed for **4**. The ^{13}C NMR spectrum (THF-d_8) of **5**-d_8 exhibited a carbon resonance at -2.3 ppm (vs -0.8 ppm for **4**), consistent with a metallacyclopentene structure. Further support for the structure of **5** was obtained from the observation that heating a sample of **5**-d_8 in acetonitrile at 60 °C (15 min) cleanly generated acetonitrile complex **4**.

In an effort to substitute an alkyne for the THF ligand in **5**, a THF (30 mL) solution of **3** (0.36 mmol) and DMAD (0.43 mmol) was heated at 60 °C for 30 min. The volatiles were then evaporated in vacuo and the residue of **5** dissolved in benzene (30 mL). Addition of DMAD (0.56 mmol) and further heating at 60 °C for 30 min led to the surprising formation of the metallacycle−alkene complex $[(Tp)Ir\{C_4(CO_2Me)_4\}(CH_2{=}CH_2)]$ (**6**) in 73% yield (Scheme 3).[8] In the ^1H NMR spectrum (C_6D_6) of **6**, a singlet was observed for the ethene hydrogens at δ 3.9 (s, 4H), and in the ^{13}C NMR spectrum (C_6D_6) the η^2-ethene and metallacycle ring-carbons gave rise to signals at 70, 150.8, and 144.2 ppm, respectively. The conversion of **5** to a metallacycle−alkene complex is not limited to DMAD. Treatment of **5** with phenylacetylene also generates a metallacyclopentadiene−alkene complex, as a single regioisomer in 68% isolated yield.

Metallacyclopentadiene−alkene and −alkyne complexes have been widely proposed as key intermediates in [2 + 2 + 2] cycloaddition reactions.[12] In a preliminary attempt to model the cycloaddition insertion step, we examined the thermolysis of **6** in toluene-d_8. Surprisingly, >96% of **6** remained after heating at 100 °C for 13 h, with no evidence for the formation of a cyclohexadiene product.

The results reported herein indicate that trispyrazolylborate ligands will provide an important entry into novel alkyne-derived metallacycles, whose analogues have only a fleeting existence in chemistry involving softer ancillary ligands. Efforts are underway to clarify the mechanism for the conversion of **5** to **6**,[13] and to enhance the reactivity of trispyrazolylmetallacycles by utilizing Tp derivatives.

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Supporting Information Available: Tables of crystallographic data for **4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Characterization data for **4**: mp 120−122 °C dec. IR (KBr) 1699 (s), 1575 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz) δ 7.72 (s, 1H), 7.66 (t, 2H, $J = 2$ Hz), 7.55 (s, 2H), 7.47 (s, 1H), 6.21 (s, 2H), 6.08 (t, 1H, $J = 2$ Hz), 3.68 (s, 3H), 3.36 (s, 3H), 2.97 (m, 2H), 2.48 (s, 3H), 2.43 (m, 1H), 2.25 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz) δ 177.7, 164.5, 157.3, 141.7, 140.6, 140.1, 139.3, 134.8, 134.7, 134.6, 114.2, 105.7, 105.3, 105.1, 51.0, 50.4, 36.9, 4.1, -0.8. Anal. Calcd for $H_{23}C_{19}N_7O_4BIr$: C, 37.02; H, 3.76. Found: C, 37.11; H, 3.85. For (**6**): mp 128−130 °C. IR (KBr) 1711(s), 1571(s), 1545(s) cm^{-1}. ^1H NMR (C_6D_6, 300 MHz) δ 8.00 (d, 1H, $J = 2.4$ Hz), 7.63 (d, 2H, $J = 2.4$ Hz), 6.97 (s, 1H), 5.78 (t, $J = 2.4$ Hz, 2H), 5.61 (t, $J = 2.4$ Hz, 1H), 3.97 (s, 4H), 3.52 (s, 6H), 3.18 (s, 6H). $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz) δ 173.4, 165.0, 150.9, 144.2, 140.4, 140.1, 135.4, 135.4, 106.2, 106.1, 70.0, 51.4, 50.9. HRMS *m/z* calcd for (M^+) $H_{26}C_{23}O_8N_6BIr$ 718.1571, obsd 718.1563.

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