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Communications

Stabilization of a Chelate Tautomer of Phenylacetylide

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Summary: Complex $[Ir(\mu\text{-}Cl)(COE)_2]_2$ (**1**; *COE* = *cis-cyclooctene) reacts with* $Li[C_5H_4(CH_2)_2N(CH_3)_2]$ *to give* $Ir\{\eta^5\text{-}C_5H_4(CH_2)_2N(CH_3)_2\}(COE)_2$ (**2**), *which affords* $IrI_2\{\eta^5\text{-}C_5,\kappa\text{-}N\text{-}[C_5H_4(CH_2)_2N(CH_3)_2]\}$ (**3**), *by addition of* I_2. *The reaction of* **3** *with phenylacetylene yields* $Ir\{\eta^5\text{-}C_5,\sigma\text{-}C^a,\sigma\text{-}C^b\text{-}[C_5H_4(CH_2)_2N(CH_3)_2C^a{=}CH\overline{C\cdots(CH)_4\cdots C^b}]\}$ (**4**), *which has been characterized by X-ray diffraction analysis.*

Electronic structures and reactivities of organic fragments change, often dramatically, when they coordinate to transition metals to form organometallic complexes. Coordination of $[RC{\equiv}C]^-$ to a late transition metal transfers the nucleophilicity from the α-carbon to the β-carbon atom.[1] X-ray[2] and reactivity[3] studies on alkynyl complexes indicate that for an adequate description of the bonding situation in this type of compounds a second zwitterionic resonance (**II** in Scheme 1) must be considered.

Scheme 1

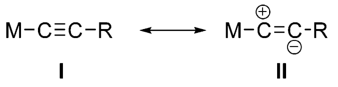
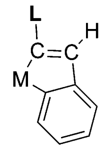


Chart 1



We desire to show that phenylacetylide has a chelate three-electron donor tautomer (Chart 1), which can be isolated by additional coordination of a Lewis base (L) at the electrophile α-carbon atom.

The new tautomer has been stabilized by coordination to the $[IrI\{\eta^5\text{-}C_5,\kappa\text{-}N\text{-}[C_5H_4(CH_2)_2N(CH_3)_2]\}]^+$ metallic fragment, which contains a 2-(dimethylamino)ethylcyclopentadienyl group. The ligands of this type are attracting increased interest in the chemistry of the metals,[4] due to the hemilabile role of the donor-nitrogen atom. Under appropriate conditions, its coordination to the metal center could stabilize highly reactive centers and have a marked influence on the catalytic properties of the active systems.[5]

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(3) Nast, R. *Coord. Chem. Rev.* **1982**, *47*, 89.

(4) (a) Jutzi, P.; Kristen, M. O.; Dahlhaus, J.; Neumann, B.; Stammler, H.-G. *Organometallics* **1993**, *12*, 2980. (b) Jutzi, P.; Kristen, M. O.; Neumann, B.; Stammler, H.-G. *Organometallics* **1994**, *13*, 3854. (c) Jutzi, P.; Dahlhaus, J. *Coord. Chem. Rev.* **1994**, *137*, 179. (d) Jutzi, P.; Siemeling, U. *J. Organomet. Chem.* **1995**, *500*, 175. (e) Philippopoulos, A. I.; Hadjiliadis, N.; Hart, C. H.; Donnadieu, B.; McGowan, P. C.; Poilblanc, R. *Inorg. Chem.* **1997**, *36*, 1842. (f) Jutzi, P.; Redeker, T. *Eur. J. Inorg. Chem.* **1998**, 663. (g) Philippopoulos, A. I.; Poilblanc, R.; Hadjiliadis, N. *Inorg. Chim. Acta* **1998**, *283*, 24. (h) Philippopoulos, A. I.; Donnadieu, B.; Poilblanc, R.; Hadjiliadis, N. *J. Organomet. Chem.* **1999**, *582*, 286.

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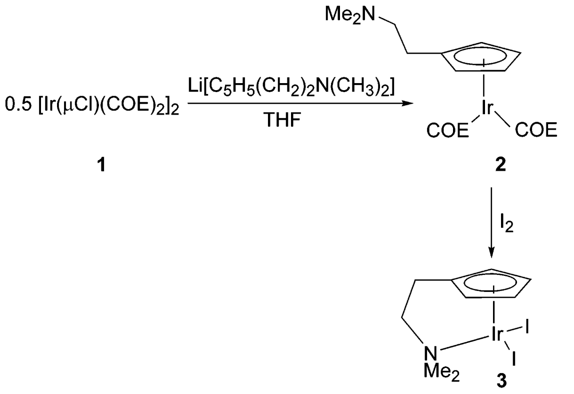
Scheme 2



The 2-(dimethylamino)ethylcyclopentadienyl ligand was introduced into the iridium atom by a procedure similar to that previously described to prepare $MI_2\{\eta^5\text{-}C_5,\kappa\text{-}N\text{-}[C_5Me_4(CH_2)_2N(CH_3)_2]\}$ (M = Rh, Ir)[4b] and $RhI_2\{\eta^5\text{-}C_5,\kappa\text{-}N\text{-}[C_5H_4(CH_2)_2N(CH_3)_2]\}$[4e] species (Scheme 2). Treatment of a tetrahydrofuran suspension of $[Ir(\mu\text{-}Cl)(COE)_2]_2$ (**1**, COE = *cis*-cyclooctene)[6] with 2.0 equiv of $Li[C_5H_4(CH_2)_2N(CH_3)_2]$[7] leads, after 5 h, to the iridium(I) derivative $Ir\{\eta^5\text{-}C_5H_4(CH_2)_2N(CH_3)_2\}(COE)_2$ (**2**), which was isolated as a pale brown oil in almost quantitative yield.[8] The addition at 0 °C of 1.0 equiv of I_2 to the dichloromethane solutions of **2** affords $IrI_2\{\eta^5\text{-}C_5,\kappa\text{-}N\text{-}[C_5H_4(CH_2)_2N(CH_3)_2]\}$ (**3**), as a red solid in about 60% yield.[9]

Figure 1 shows a view of the molecular structure of **3**. The geometry around the iridium center is close to octahedral, with the cyclopentadienyl group occupying three sites of a face. The Ir–N distance (2.206(5) Å) and the Ir–I bond lengths (2.6950(5) and 2.7006(5) Å) compare well with those reported for the related compound $IrI_2\{\eta^5\text{-}C_5,\kappa\text{-}N\text{-}[C_5Me_4(CH_2)_2N(CH_3)_2]\}$.[4b]

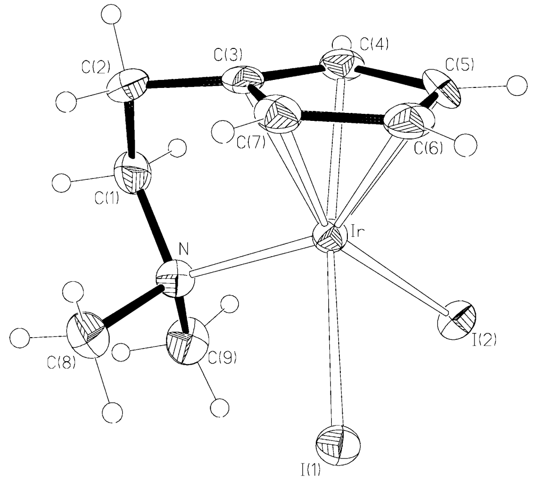
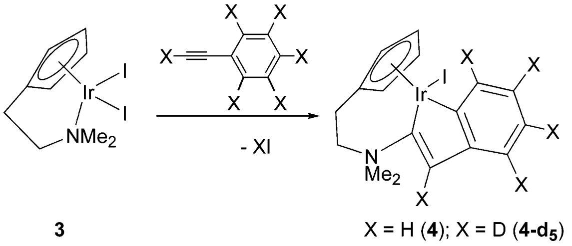


Figure 1. Molecular diagram of complex **3**. Selected bond distances (Å) and angles (deg): Ir–I(1) 2.6950(5), Ir–I(2) 2.7006(5), Ir–N 2.206(5); M–Ir–I(1) 127.0, M–Ir–I(2) 125.0, M–Ir–N 117.0, I(1)–Ir–I(2) 89.811(15), I(1)–Ir–N 92.88(12), I(2)–Ir–N 96.87(12). (M is the midpoint of the Cp ligand.)

The reaction of **3** with phenylacetylene in tetrahydrofuran or dichloromethane at room temperature gives, after 16 h, the complex containing the tautomer shown in Chart 1.[10] This novel derivative (**4** in eq 1) was isolated as a pale brown solid in about 45% yield.[11] Although the elementary steps of the process are not clear, the formation of **4** appears to occur through a 1,3-hydrogen shift from an ortho-aryl proton of the aromatic ring to the β-carbon atom of the alkyne. Thus, we have observed that, in dichloromethane-d_2, the reaction of **3** with Ph-d_5-C≡CD gives rise to **4**-d_5, with a deuterium at the β-carbon atom of the alkenyl unit, while in dichloromethane or dichloromethane-d_2 the reaction of **3** with Ph-C≡CD affords **4**, containing a hydrogen atom at the β-carbon atom of the alkenyl unit.



(1)

Complex **4** has been characterized by an X-ray crystallographic study. The structure has two chemically equivalent but crystallographically independent molecules of complex **4** in the asymmetric unit. A drawing of one of them (molecule **a**) is shown in Figure 2. As for **3**, the geometry around the iridium atom is close to octahedral, with the cyclopentadienyl group occupying three sites of a face. The bidentate unit of the polydentate carbon-donor ligand, which acts with a bite angle of 77.6(3)° in molecule **a** and 77.8(3)° in molecule **b**, forms a five-membered ring with the metal. The distances Ir–C(1) and Ir–C(4) (Ir–C(18) and Ir–C(21) in molecule **b**) are 1.997(8) and 2.041(7) Å (2.005(8) and 2.041(8) Å, in molecule **b**), respectively.

The bonding situation at C(1) (C(18) in molecule **b**) can be rationalized as a result of the σ-donation from a filled sp²-orbital of C(1) to the metal and the σ-donation of the lone pair of the amine to an empty sp²-orbital of C(1). In agreement with a sp² hybridization for this atom, the angles around it are close to 120°. The coordination of the amine group to C(1) (C(18) in molecule **b**) is strongly supported by the N(1)–

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(8) Spectroscopic data for **2**: ^1H NMR (C_6D_6, 20°C): δ 4.86 (m, 2H, C_5H_4), 4.44 (m, 2H, C_5H_4), 2.49 (m, 4H, =CH, COE), 2.25 (br, 4H, CH_2-CH_2–N), 2.14 (s, 6H, NMe_2), 1.74–1.28 (m, 24H, CH_2, COE). ^{13}C NMR (C_6D_6, 20°C): δ 102.1 (C_{ipso}, C_5H_4), 86.7 (C_5H_4), 86.5 (C_5H_4), 62.1 (NCH_2), 46.0 (NMe_2), 45.5 (=CH, COE), 33.7 (CH_2, COE), 33.3 (CH_2, COE), 26.8 (CH_2, COE), 26.3 (CH_2–Cp).

(9) Spectroscopic data for **3**: ^1H NMR (CD_2Cl_2, 20 °C): δ 5.83 (m, 2H, C_5H_4), 5.59 (m, 2H, C_5H_4), 3.82 (t, 6.3 Hz, 2H, CH_2CH_2), 3.16 (s, 6H, NMe_2), 2.43 (t, 6.3 Hz, 2H, CH_2CH_2). ^{13}C NMR (CD_2Cl_2, 20 °C plus APT): 106.0 (C_{ipso}, C_5H_4), 82.0 (NCH_2), 76.6 (C_5H_4), 74.7 (C_5H_4), 57.5 (NMe_2), 25.0 (CH_2–Cp).

(10) We note that Werner has previously reported the insertion of a CH_2 unit in the Ir–N bond of the complex *trans*-$IrCl\{\kappa\text{-}P\text{-}[^iPrP(CH_2)_2N(CH_3)_2]\}\{\kappa\text{-}P,\kappa\text{-}N\text{-}[^iPrP(CH_2)_2N(CH_3)_2]\}$ to give a species containing the Ir–CH_2–N moeity. See: Werner, H.; Schulz, M.; Windmüller, B. *Organometallics* **1995**, *14*, 3659.

(11) Spectroscopic data for **4**: ^1H NMR (CD_2Cl_2, 20 °C): δ 7.71 (psd, 1H, C_6H_4), 7.16 (psd, 1H, C_6H_4), 6.88 (s, 1H, =CH), 6.74 (pst, 1H, C_6H_4), 6.61 (pst, 1H, C_6H_4), 5.56 (m, 1H, C_5H_4), 5.47 (m, 1H, C_5H_4), 5.18 (m, 1H, C_5H_4), 4.47 (m, 1H, C_5H_4), 3.50 (s, 3H, NMe), 3.46 (m, 2H, CH_2-CH_2), 3.45 (s, 3H, NMe), 2.91 (m, 2H, CH_2CH_2). ^{13}C NMR (CD_2Cl_2, 20 °C plus APT): 163.4 (Ir–C), 160.4 (Ir–C), 153.2 (C_{ipso}, C_6H_4), 140.5 (=CH), 130.6, 123.8, 123.4, 121.6, (CH, C_6H_4), 90.9 (2C, C_5H_4), 90.4 (C_{ipso}, C_5H_4), 85.2 (C_5H_4), 84.5 (C_5H_4), 70.3 (CH_2N), 61.1 (NMe), 52.3 (NMe), 22.2 (CH_2Cp).

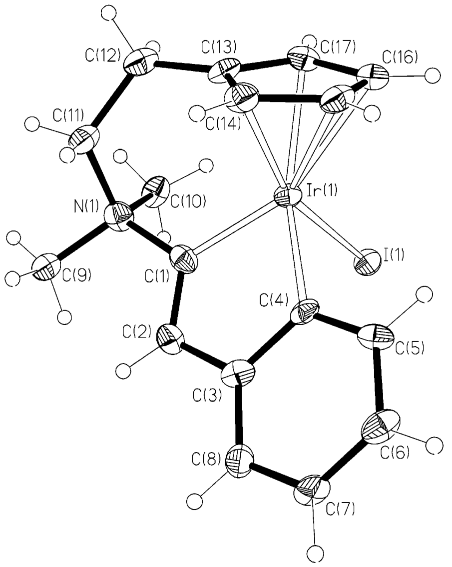

Figure 2. Molecular diagram of complex **4**. Selected bond distances (Å) and angles (deg) for the two independent molecules: Ir(1)−I(1) 2.6785(6) **a**, 2.6755(6) **b**, Ir(1)−C(1) 1.997(8) **a**, 2.005(8) **b**, Ir(1)−C(4) 2.041(7) **a**, 2.041(8) **b**, C(1)−C(2) 1.331(10) **a**, 1.339(10) **b**, M(1)−Ir(1)−I(1) 126.6 **a**, 126.1 **b**, M(1)−Ir(1)−C(1) 127.3 **a**, 127.0 **b**, M(1)−Ir(1)−C(4) 131.0 **a**, 131.7 **b**, I(1)−Ir(1)−C(1) 91.0(2) **a**, 91.4(2) **b**, I(1)−Ir(1)−C(4) 87.8(2) **a**, 87.6(2) **b**, C(1)−Ir−C(4) 77.6(3) **a**, 77.8(3) **b**, N(1)−C(1)−C(2) 119.4(7) **a**, 118.8(7) **b**, C(1)−C(2)−C(3) 112.9(7) **a**, 111.2(7) **b**. (M(1) is the midpoint of the Cp ligand.)

C(1) distance (N(2)−C(18) in molecule **b**) of 1.516(10) Å (1.518(9) Å in molecule **b**), which is statistically identical with the other N−C bond lengths present in the corresponding molecule. The presence of a carbon−carbon double bond between C(1) and C(2) (C(18) and C(19) in molecule **b**) is supported by the separation between them, 1.331(10) Å (1.338(10) Å in molecule **b**).

The most noticeable spectroscopic features of **4** are in the ^{1}H NMR spectrum a singlet at 6.89 ppm, corresponding to the C(2)−H proton, and in the ^{13}C{^{1}H} NMR spectrum two weak resonances at 163.4 and 160.4 ppm assigned to the carbon atoms attached to the iridium center.

In conclusion, the reaction of the iridium(III) complex $IrI_2\{\eta^5\text{-}C_5,\kappa\text{-}N\text{-}[C_5H_4(CH_2)_2N(CH_3)_2]\}$ (**3**) with phenylacetylene affords the novel derivative $Ir\{\eta^5\text{-}C_5,\sigma\text{-}C^a,\sigma\text{-}C^b\text{-}[C_5H_4(CH_2)_2N(CH_3)_2C^a{=}CH\overline{C\overset{..}{-}(CH)_4\overset{..}{-}C^b}]\}$ (**4**) containing a polydentate ligand (formally pentadentate) without precedents. The fragment $C^a{=}CH\overline{C\overset{..}{-}(CH)_4\overset{..}{-}C^b}$ of this ligand can be described as a bidentate three-electron donor tautomer of phenylacetylide.

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Supporting Information Available: Experimental details and structural data related with the synthesis and characterization of the complexes **2**, **3**, and **4**. Tables of atomic coordinates and equivalent isotropic displacement coefficients, anisotropic thermal parameters, experimental details of the X-ray studies, and bond distances and angles for **3** and **4**. This material is available free of charge via the Internet at http://www.pubs.acs.org.

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