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Unassisted η^2-Coordination of Polycyclic Aromatic Hydrocarbons to Platinum(II)

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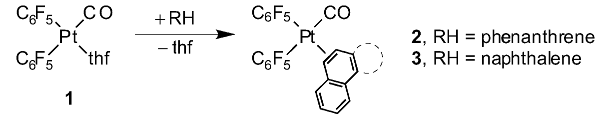
The coordination of phenanthrene to the d^8 Pt^{II} center in (*SP*-4-2)-[$Pt(C_6F_5)_2(CO)(\eta^2\text{-}C_{14}H_{10})$] causes a slight pyramidalization at the metal-bound C atoms (C^9 and C^{10}), but no perceptible elongation of the corresponding C–C bond [C(13)–C(14) 132.0(5) *vs.* 133.8(5) pm in the free ligand].

Efficient hydrocarbon C−H activation is among the most pursued goals in modern chemistry.[1] Late transition metal complexes of various kinds (especially of Pt^{II})[1,2] are known to accomplish a number of such processes under unusually mild conditions, thereby inducing a higher degree of selectivity. Much effort has been devoted to studying the key steps of the mechanism involved, a better understanding of which would enable the design and development of new systems with enhanced activity and/or selectivity. It is currently agreed that the first step in Pt^{II}-mediated arene C−H activation entails the formation of an intermolecular η^2-arene complex.[3,4] Unless assisted by intramolecular coordination of a pendant donor substituent[5]—thus benefiting from the chelate effect—this coordination mode is still rare in Pt^{II} chemistry and, in fact, it has only recently been unambiguously established.[3,6] Here we report on highly unusual Pt^{II} species containing η^2-coordinated condensed arenes.

Scheme 1. Synthesis of Compounds **2** and **3**



The square-planar (*SP*-4) complex *cis*-[$Pt(C_6F_5)_2(CO)(thf)$] (**1**) reacts with phenanthrene ($C_{14}H_{10}$) in CH_2Cl_2 solution (Scheme 1) under substitution of the weakly coordinated thf molecule and formation of *cis*-[$Pt(C_6F_5)_2(CO)(\eta^2\text{-}C_{14}H_{10})$] (**2**). In a similar way, **1** reacts with naphthalene ($C_{10}H_8$) in CH_2ClCH_2Cl solution to give *cis*-[$Pt(C_6F_5)_2(CO)(\eta^2\text{-}C_{10}H_8)$] (**3**). Compounds **2** and **3** can be isolated as white solids in moderate yields (see Supporting Information for details).

The molecular structure of **2** was established by single-crystal X-ray analysis. The Pt center is located in a *SP*-4 environment (Figure 1) defined by the C-donor atoms of the C_6F_5 and CO ligands and the midpoint between the two metal-coordinated phenanthrene C atoms. The ligands adopt a *cis* arrangement as in the parent species so the substitution reaction in Scheme 1 takes place with stereoretention. Two strong absorptions assignable to the X-sensitive vibration modes of the C_6F_5 groups[7] are accordingly observed in the IR spectra of both **2** and its parent species **1** (C_{2v} local symmetry; IR-active X-sensitive modes: $A_1 + B_1$). Phenanthrene coordinates to the "*cis*-$Pt(C_6F_5)_2(CO)$" moiety in an essentially symmetric form [Pt−C(13) 234.5(3), Pt−C(14) 231.2(3) pm] through the two C atoms (C^9 and C^{10} in standard IUPAC notation)[8] for which the highest π-electron density has been calculated by Hückel MO methods.[9] Coordination through C^9 and C^{10} also involves the lower loss of aromaticity in the phenanthrene ligand measured in terms

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(1) Labinger, J. A. *J. Mol. Catal. A* **2004**, *220*, 27. Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507. Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2437. Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879. Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154.

(2) (a) Lersch, M.; Tilset, M. *Chem. Rev.* **2005**, *105*, 2471. (b) Fekl, U.; Goldberg, K. I. *Adv. Inorg. Chem.* **2003**, *54*, 259. (c) Stahl, S. S.; Labinger, J. A.; Bercaw, J. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 2180.

(3) Norris, C. M.; Reinartz, S.; White, P. S.; Templeton, J. L. *Organometallics* **2002**, *21*, 5649.

(4) Johansson, L.; Tilset, M.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 10846.

(5) Alonso, E.; Forniés, J.; Fortuño, C.; Martín, A.; Orpen, A. G. *Organometallics* **2003**, *22*, 2723. Alonso, E.; Forniés, J.; Fortuño, C.; Martín, A.; Orpen, A. G. *Organometallics* **2000**, *19*, 2690. Wright, L. L.; Moore, S. J.; McIntyre, J. A.; Dowling, S. M.; Overcast, J. D.; Grisel, G. R., IV.; Nelson, K. K.; Rupert, P. R.; Pennington, W. T. *Organometallics* **1999**, *18*, 4558. Casas, J. M.; Forniés, J.; Martínez, F.; Rueda, A. J.; Tomás, M.; Welch, A. J. *Inorg. Chem.* **1999**, *38*, 1529. Ara, I.; Falvello, L. R.; Forniés, J.; Lalinde, E.; Martín, A.; Martínez, F.; Moreno, M. T. *Organometallics* **1997**, *16*, 5392. Casas, J. M.; Forniés, J.; Martín, A.; Menjón, B.; Tomás, M. *J. Chem. Soc., Dalton Trans.* **1995**, 2949. Casas, J. M.; Forniés, J.; Martín, A.; Menjón, B. *Organometallics* **1993**, *12*, 4376. Forniés, J.; Menjón, B.; Gómez, N.; Tomás, M. *Organometallics* **1992**, *11*, 1187.

(6) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 12724.

(7) Usón, R.; Forniés, J. *Adv. Organomet. Chem.* **1988**, *28*, 219.

10.1021/ic050405q CCC: $30.25

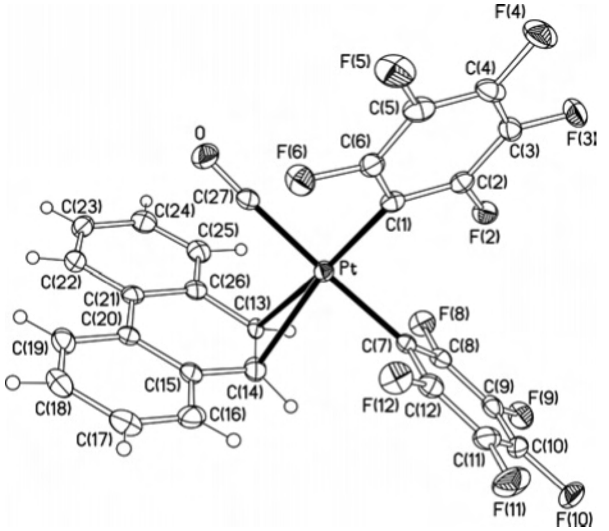
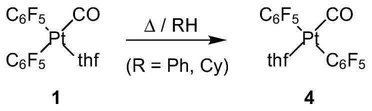


Figure 1. Thermal ellipsoid diagram of **2**. Selected distances (pm) and angles (deg): Pt−C(1), 203.4(3); Pt−C(7), 204.0(3); Pt−C(13), 234.5(3); Pt−C(14), 231.2(3); Pt−C(27), 193.7(3); C(13)−C(14), 132.0(5); C(27)−O, 111.8(4); C(1)−Pt−C(7), 88.64(11); C(1)−Pt−C(27), 89.14(12); C(7)−Pt−C(27), 177.78(11); Pt−C(27)−O, 177.9(3).

of resonance energy.[10] The C(13)−C(14) line forms an angle of 21.2° with the normal to the coordination plane and adopts a staggered conformation with respect to the *trans*-standing C_6F_5 group. It is interesting to note that the C^9-C^{10} bond distance in **2** [C(13)−C(14) 132.0(5) pm] is statistically indistinguishable from the corresponding one in the free ligand [133.8(5) pm];[11] hence, no elongation at all is observed upon coordination. This structural feature denotes that little π-back-donation, if any, from the "*cis*-$Pt(C_6F_5)_2(CO)$" moiety to the antibonding π^* aromatic system of phenanthrene actually occurs. This can be considered to be a consequence of the marked electron-withdrawing character of the C_6F_5 groups,[12] as well as the well-known ability of CO to behave as a poor σ-donor/good π-acceptor ligand. The high ν_{CO} value observed in the IR spectrum of **2**, $\nu_{CO} = 2125$ cm^{-1}, can be taken as further evidence of the lack of electron density at the metal center.[13] In this context, it is interesting to note that a significant lengthening of the coordinated C−C bond [C^9-C^{10} 146.0(5) pm] was observed in [Rh(η^5-C_5Me_5)(PMe_3)(η^2-$C_{14}H_{10}$)].[15] This observation would be in agreement with the higher electron density available for the Rh center considering: (1) its lower oxidation state and (2) the more marked basicity of the remaining ligands. It is also interesting to note that considerably shorter Pt−C distances [221(1)−227(1) pm] have been found in other Pt^{II} compounds containing η^2-arene ligands, [PtH(HTp′)(η^2-RH)]$^+$ [RH = benzene, *p*-xylene; Tp′ = hydridotris(3,5-dimethylpyrazolyl)borato].[3,6] In these structurally characterized precedents, a slight lengthening of the η^2-coordinated C−C bond was also observed.

Scheme 2. Isomerization of (cis) **1** to (trans) **4**



The presence of two sets of C_6F_5 signals in the ^{19}F NMR spectrum of **2** in [^2H]dichloromethane solution between −80 and 25 °C denotes the presence of two chemically inequivalent C_6F_5 groups, in agreement with the *cis* arrangement observed in the solid-state structure. Despite the negligible structural changes observed in the C framework with respect to the free ligand, the coordination of phenanthrene to the "*cis*-$Pt(C_6F_5)_2(CO)$" moiety produces a distinct upfield shift in the resonance signal assigned to H^9 and H^{10}, which appear in the ^1H NMR spectrum of **2** as a singlet with platinum satellites [$^2J(^{195}Pt,H) = 48$ Hz] at $\delta = 7.51$ ppm (*cf.* $\delta = 7.78$ ppm for free phenanthrene). This fact can be related to the slight pyramidalization observed at the coordinated C atoms, whose corresponding C−H bonds deviate more than 10° from the phenanthrene ring, implying a higher contribution of the 2p orbitals in the sp^n hybridization of C^9 and C^{10} atoms. However, no significant modification in the corresponding $^1J(^{13}C,H)$ value has been observed (167 *vs.* 160 Hz in the free ligand).

It has been recently pointed out[14] that metal-promoted C−H activation processes should be favored by the enhanced Lewis-basicity of the "ML_n" metal fragment. On the other hand, the required coordination of the organic substrate RH would be expected to preferentially occur at highly acidic metal complex species. A mismatch in properly balancing these two opposite electronic requirements in the "*cis*-$Pt(C_6F_5)_2(CO)$" fragment could well be the reason **2**, containing an η^2-coordinated phenanthrene molecule, is sufficiently stable to allow its isolation and extensive characterization while, in turn, C−H activation has not yet been observed to occur. These results can be considered to exemplify the electrophilic behavior of electron-poor metal centers.[2a]

In contrast to the previously dicussed "electrophilic behavior" observed for the "*cis*-$Pt(C_6F_5)_2(CO)$" fragment toward the polycyclic aromatic hydrocarbons, it has been found that benzene is not to accomplish clean substitution of thf in complex **1**. Thus, heating **1** in benzene solution at 50−60 °C for 1 h results in an isomerization process giving *trans*-[$Pt(C_6F_5)_2(CO)(thf)$] (**4**) in 50% yield together with extensive decomposition to platinum metal (Scheme 2). The same isomerization process has been found to occur using cyclohexane as solvent. In this saturated hydrocarbon, however, the yield of isolated **4** increases to 70% and no

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(8) Rigaudy, J.; Klesney, S. P. *Nomenclature of Organic Chemistry*; Pergamon Press: Oxford, UK, 1979.

(9) Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 11655.

(10) Chin, R. M.; Dong, L.; Duckett, S. B.; Partridge, M. G.; Jones, W. D.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7685.

(11) Petříček, V.; Císařová, I.; Hummel, L.; Kroupa, J.; Březina, B. *Acta Crystallogr., Sect. B* **1990**, *46*, 830.

(12) Sheppard, W. A. *J. Am. Chem. Soc.* **1970**, *92*, 5419. Tolman, C. A. *J. Am.* Chem. Soc. **1970**, *92*, 2953.

(13) The ν_{CO} value in **2** is even higher than that found in the cationic complexes [PtMe(RN=CR′−CR′=NR-κ^2N)(L)][BF_4] (L = CO; R = an aryl group; R′ = H, Me; $\nu_{CO} = 2103-2113$ cm^{-1}), whose corresponding solvates (L = H_2O, CF_3CH_2OH) have been found to effectively promote the activation of benzene C−H bonds.[14]

(14) Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 1378.

(15) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1989**, *111*, 8722.

decomposition to Pt^0 is observed (even though the temperature was maintained in this case at 90−95 °C). In view of the different outcome, it might be considered that the solvent plays a noninnocent role.

Further studies aiming to exploit the synthetic potential of the *cis* and *trans* “$Pt(C_6F_5)_2(CO)$” moieties as highly acidic, single-site metal fragments enabling unusual coordination patterns are currently underway.

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Supporting Information Available: Crystallographic data of **2** (CIF) and experimental details for the preparation of **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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