

Unassisted η^2 -Coordination of Polycyclic Aromatic Hydrocarbons to Platinum(II)Jesús R. Berenguer,[†] Juan Forniés,* L. Francisco Martín, Antonio Martín, and Babil Menjón

Instituto de Ciencia de Materiales de Aragón, Facultad de Ciencias, Universidad de Zaragoza-C.S.I.C., C/Pedro Cerbuna 12, E-50009 Zaragoza, Spain

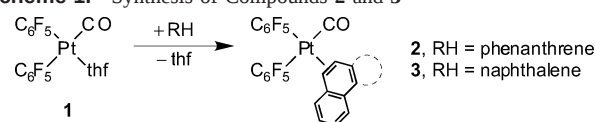
Received March 18, 2005

The coordination of phenanthrene to the d^8 Pt^{II} center in (SP-4)-2-[Pt(C₆F₅)₂(CO)(η^2 -C₁₄H₁₀)] causes a slight pyramidalization at the metal-bound C atoms (C⁹ and C¹⁰), 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 substituent⁵—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.

The square-planar (SP-4) complex *cis*-[Pt(C₆F₅)₂(CO)(thf)] (**1**) reacts with phenanthrene (C₁₄H₁₀) in CH₂Cl₂ solution (Scheme 1) under substitution of the weakly coordinated thf

Scheme 1. Synthesis of Compounds 2 and 3



molecule and formation of *cis*-[Pt(C₆F₅)₂(CO)(η^2 -C₁₄H₁₀)] (**2**). In a similar way, **1** reacts with naphthalene (C₁₀H₈) in CH₂ClCH₂Cl solution to give *cis*-[Pt(C₆F₅)₂(CO)(η^2 -C₁₀H₈)] (**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 C₆F₅ 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 C₆F₅ groups⁷ 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(C₆F₅)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 (C⁹ and C¹⁰ in standard IUPAC notation)⁸ for which the highest π -electron density has been calculated by Hückel MO methods.⁹ Coordination through C⁹ and C¹⁰ also involves the lower loss of aromaticity in the phenanthrene ligand measured in terms

* To whom correspondence should be addressed.

[†] Current address: Departamento de Química, Grupo de Síntesis Química de la Rioja, UA-CSIC, Universidad de La Rioja, C/Madre de Dios 51, E-26006 Logroño (La Rioja), Spain.

- (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.

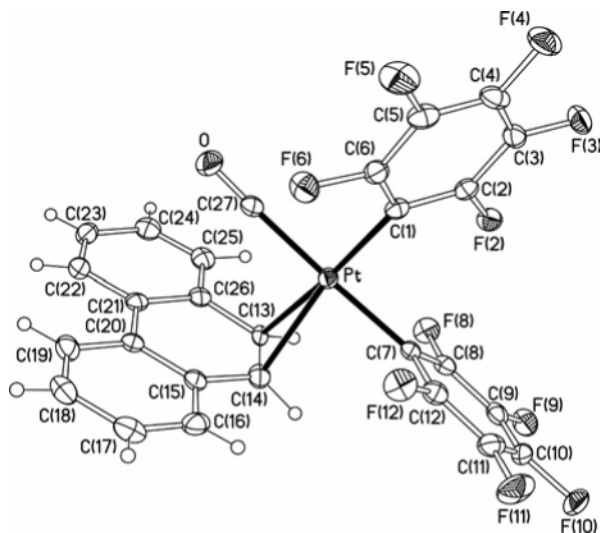
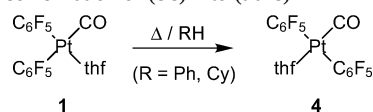


Figure 1. Thermal ellipsoid diagram of **2**. Selected distances (pm) and angles (deg): Pt–C(1), 203.4(3); Pt–C(7), 204.0(3); Pt–C(13), 234.5(3); Pt–C(14), 231.2(3); Pt–C(27), 193.7(3); C(13)–C(14), 132.0(5); C(27)–O, 111.8(4); C(1)–Pt–C(7), 88.64(11); C(1)–Pt–C(27), 89.14(12); C(7)–Pt–C(27), 177.78(11); 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 C₆F₅ group. It is interesting to note that the C⁹–C¹⁰ 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(C₆F₅)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 C₆F₅ 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**, $\nu_{\text{CO}} = 2125 \text{ cm}^{-1}$, 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 [C⁹–C¹⁰ 146.0(5) pm] was observed in [Rh(η^5 -C₅Me₅)(PMe₃)(η^2 -C₁₄H₁₀)].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

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



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.

The presence of two sets of C₆F₅ signals in the ¹⁹F NMR spectrum of **2** in [²H]dichloromethane solution between –80 and 25 °C denotes the presence of two chemically inequivalent C₆F₅ 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(C₆F₅)₂(CO)” moiety produces a distinct upfield shift in the resonance signal assigned to H⁹ and H¹⁰, which appear in the ¹H NMR spectrum of **2** as a singlet with platinum satellites [²*J*(¹⁹⁵Pt,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 sp² hybridization of C⁹ and C¹⁰ atoms. However, no significant modification in the corresponding ¹*J*(¹³C,H) value has been observed (167 *vs.* 160 Hz in the free ligand).

It has been recently pointed out¹⁴ 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-(C₆F₅)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 discussed “electrophilic behavior” observed for the “*cis*-Pt(C₆F₅)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(C₆F₅)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

- (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.; Čisářová, 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^2 N)(L)][BF₄] (L = CO; R = an aryl group; R' = H, Me; $\nu_{\text{CO}} = 2103$ –2113 cm^{–1}), whose corresponding solvates (L = H₂O, CF₃CH₂OH) 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* “ $\text{Pt}(\text{C}_6\text{F}_5)_2(\text{CO})$ ” moieties as highly acidic, single-site metal fragments enabling unusual coordination patterns are currently underway.

Acknowledgment. This work was supported by the Spanish MCYT (DGI)/FEDER (Project No. BQU2002-03997-CO2-02) and Promerus LLC.

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>.

IC050405Q