An Ir(III) Compound That Thermally Activates Two Molecules of C_6H_6 and Forms a Stable Dinitrogen Complex

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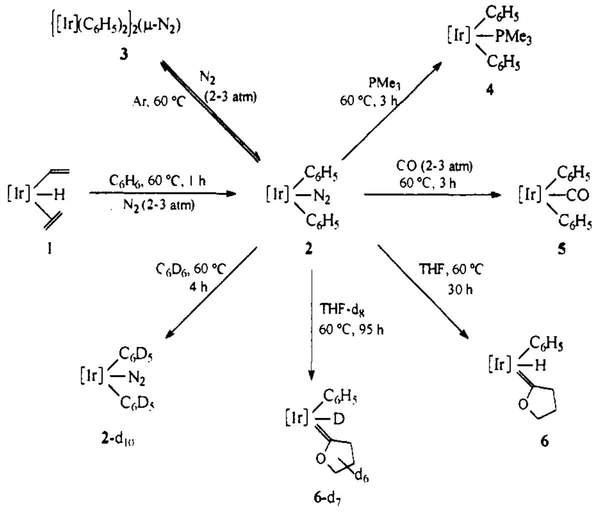
Received September 10, 1993

The study of intermolecular C–H bond activation reactions of hydrocarbons with transition-metal compounds is an active area of research.[1] We reported recently that the Ir(III) complex Tp*Ir($CH{=}CH_2$)(H)(C_2H_4) (**1**) (Tp* = HB(3,5-Me_2-pz)$_3$), generated thermally or photochemically from the bis(ethylene) isomer Tp*Ir$(C_2H_4)_2$, regioselectively activates the two α-C–H bonds of cyclic ethers (e.g., THF) with formation of complexes containing a hydride, an alkyl, and an oxycarbene functionality.[2] Now we report that **1** is also able to activate two molecules of C_6H_6 and that this unusual transformation involves, in addition, the coordination of N_2 with formation of the thermally stable complexes Tp*Ir$(C_6H_5)_2(N_2)$ (**2**) and [Tp*Ir$(C_6H_5)_2]_2(\mu$-$N_2)$ (**3**), the latter of which has been structurally authenticated by X-ray crystallography.

Heating a solution of **1** in C_6H_6 (see Scheme 1 for reaction conditions) affords high yields of the white crystalline complex **2**,[3] together with small amounts of the sparingly soluble **3** and a volatile mixture of C_2H_6 and C_2H_4 (1:1 ratio by NMR). The presence of the coordinated N_2 ligand in **2** and **3** is evidenced by a strong absorption at 2190 cm^{-1} in the IR spectrum of **2** and at 2130 cm^{-1} in the Raman spectrum of the binuclear derivative **3**. These compounds are remarkable for two reasons: first, they constitute very rare examples of thermally robust Ir(III)–N_2 complexes,[4] and second, their formation involves *the activation of two molecules of C_6H_6* by a single metal site. Benzene C–H bond activation is well documented,[1,5] but the transformation reported here has only very rarely been observed in related Cp′ systems[6] (Cp′ = any cyclopentadienyl ligand).

Under the conditions stated in Scheme 1, an equilibrium between **2** and **3** that allows the preparation of larger quantites of the latter complex can be established. Single crystals of **3** have been obtained; Figure 1 shows a partial ORTEP representation of its molecules including the atom labeling scheme and some relevant bonding parameters.[7] The two Tp*Ir$(C_6H_5)_2$ moieties, which are not related by symmetry, are almost linearly bridged by the N_2 ligand (Ir–N–N = 174(2)°), which exhibits a very short N–N separation (1.13(3) Å), close to that of free N_2 (1.097 Å). To our knowledge, this is the first Ir–N_2 complex structurally characterized by X-ray methods.

Scheme 1



[Ir] = Tp*Ir

The N_2 ligand in **2** is labile and can be thermally replaced by other ligands like PMe_3 or CO with formation of the bis(aryl) adducts **4** and **5**, respectively (Scheme 1). Complex **2** is also capable of activating arenes: treatment with C_6D_6 affords the fully deuterated complex **2**-d_{10}. An interesting reaction ensues in the presence of THF to give the Fischer-type Ir(III) alkylidene complex **6**.[8] That this reaction does not proceed through the intermediacy of a lower-valence benzyne complex, as in other bis(aryl) systems capable of C–H activation,[5h,6a,b,9] is demonstrated

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(3) Characterization data for **2**: IR (Nujol mull) 2190 (s) $\nu_{N\equiv N}$; ^{1}H NMR (C_6D_6, 500 MHz) δ 1.14, 1.56, 2.09, 2.14 (s, 1:2:1:2 ratio, 6 C-Me), 5.47, 5.51 (s, 1:2 ratio, 3 C-H pz), 6.56, 6.79, 7.03, 7.31, 8.31 (dt, td, tt, td, dt, respectively, 1:1:1:1:1 ratio, 2 equiv C_6H_5). Anal. Calcd for **2**: C, 48.3; H, 4.8; N, 16.7. Found: C, 47.5; H, 4.9; N, 15.9.

(4) N_2 complexes of Ir(III) are rare, and they are usually thermally unstable. See, for example: Bauer, H.; Beck, W. *J. Organomet. Chem.* **1986**, *308*, 73. Blake, D. M. *J. Chem. Soc., Chem. Commun.* **1974**, 815. Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589. Henderson, R. A.; Leigh, G. J.; Pickett, C. J. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 197.

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(6) Early transition metals diaryls, e.g., $Cp_2Zr(Ar)_2$, can undergo C–H σ-bond metathesis in the presence of aromatic substrates.[6a] A highly electrophilic f-metal system has been shown to activate two molecules of C_6H_6,[6b,c] and some Cp*IrMe_2(L) complexes undergo a similar transformation after being heated at high temperatures.[6d,e] (a) Erker, G. *J. Organomet. Chem.* **1977**, *134*, 189. (b) Fendrick, C. M.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 425. (c) Bruno, J. W.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7357. (d) Gómez, M.; Yarrow, P. I. W.; Robinson, D. J.; Maitlis, P. M. *J. Organomet. Chem.* **1985**, *279*, 115. (e) Diversi, P.; Iacoponi, S.; Ingrosso, G.; Laschi, F.; Lucherini, A.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1993**, 351.

(7) Crystal structure data for **3**: formula = $C_{54}H_{62}B_2N_{14}Ir_2$, FW = 1314, monoclinic, space group $C2/c$, a = 54.89(2) Å, b = 10.920(5) Å, c = 19.791(7) Å, β = 91.90°, V = 11856(1) Å^3, Z = 8. Anisotropic refinement of all non-hydrogen atoms. 5123 unique data with $I \geq 2\sigma(I)$. R = 0.063 and R_w = 0.082.

(8) Characterization data for **6**: IR (Nujol mull) 2130 (s) ν_{Ir-H}; ^{1}H NMR (C_6D_6, 500 MHz) δ −17.31 (s, Ir-H); $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz) δ 22.1 ($CH_2CH_2CH_2$), 55.6 ($Ir{=}CCH_2$), 79.3 (OCH_2), 262.7 (Ir=C<). Anal. Calcd for **6**: 47.0; H, 5.4; N, 13.2. Found: C, 46.9; H, 5.3; N, 13.0.

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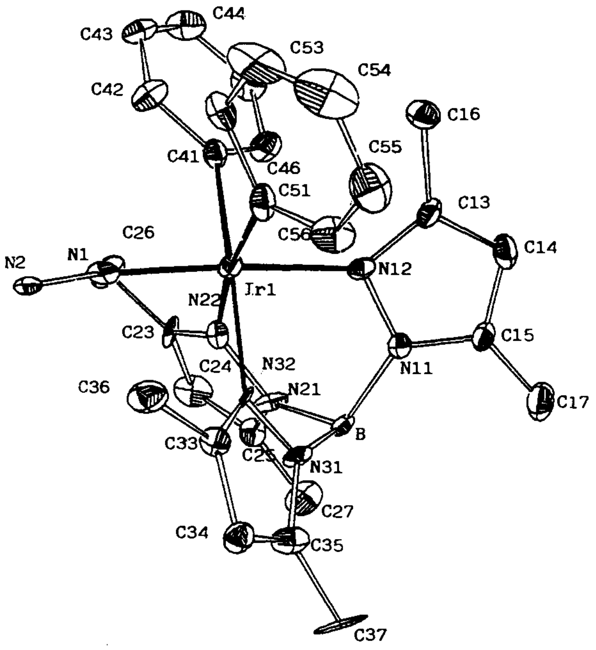

Figure 1. Partial view of the structure of 3 showing only a Tp*Ir$(C_6H_5)_2$-(μ-N_2) fragment (the other Tp*Ir$(C_6H_5)_2$ entity has been omitted for clarity. Selected bond distances (Å) and angles (deg) within the Ir(1)-N(1)-N(2)-Ir(2) unit: Ir(1)-N(1), 1.93(2); N(1)-N(2), 1.13(3); Ir(2)-N(2), 1.94(2); Ir(1)-N(1)-N(2), 174(2).

by isotopic labeling experiments: the reaction of **2**-d_0 with THF-d_8 provides the deuteride complex **6**-d_7 plus C_6H_5D.

Although a detailed kinetic and mechanistic study is still under way, some relevant information about the course of this interesting transformation can be deduced from trapping experiments carried out with variable amounts of PMe_3 and a ca. 0.09 M benzene solution of **1**. This has demonstrated the formation of three intermediate species, namely "Tp*Ir$(C_2H_5)(CH{=}CH_2)$" (**A**), "Tp*Ir$(CH{=}CH_2)(C_6H_5)$" (**B**) (both likely containing a coordinated η^2-C_6H_6 ligand), and "Tp*Ir$(C_6H_5)_2(C_2H_4)$" (**C**), which can be trapped in the form of the corresponding PMe_3 adducts in the cases of **A** and **B** and in the form of the sparingly soluble ylidic species Tp*Ir$(C_6H_5)_2(CH_2CH_2PMe_3)$ (**7**)[10] in the case of **C**. It is worth mentioning at this point that in order to trap intermediate **A** (or **B**) as efficiently as **C**, a very high concentration of PMe_3 (ca. 1:1 C_6H_6:PMe_3 solvent mixture) is needed. Since, in the absence of the aromatic hydrocarbon, **A** can be readily trapped by Lewis bases (PMe_3, donor solvents like CH_3CN, DMSO[2,11]), this proves the high efficiency of this system for the activation of the C–H bonds of C_6H_6. Whether or not the transformations reported in this paper involve Ir(V) intermediates[12] resulting from C–H oxidative additions to the Ir(III) center,[13] as opposed to concerted H transfers without change in the oxidation state of the metal, cannot be presently ascertained and requires more experimental studies that will be developed in the near future.

Acknowledgment. We thank the Dirección General de Investigación Científica y Técnica for the support of this research (Project No. PB90-0890). M.C.N. thanks the Ministerio de Educación y Ciencia for a Predoctoral Fellowship. We also thank the University of Seville for the use of NMR and analytical facilities.

Supplementary Material Available: Tables of positional parameters, thermal parameters, bond lengths and bond angles, and crystal data for 3 (6 pages); listing of observed and calculated structure factors (35 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(10) Characterization data for **7**: ^{1}H NMR (DMSO-d_6, 300 MHz) δ 0.68, 1.20, 2.38, 2.39 (s, 1:2:2:1 ratio, 6 Me-C), 1.13, 1.91 (m, CH_2PMe_3 and Ir-CH_2), 1.57 (d, $^2J_{HP}$ = 14 Hz, PMe_3), 5.66, 5.74 (s, 2:1 ratio, 3 C-H pz), 6.2–7.6 (m, C_6H_5); $^{13}C\{^1H\}$ NMR (DMSO-d_6, 75 MHz) δ –17.0 (b r s, Ir-CH_2), 7.0 (d, $^1J_{CP}$ = 53 Hz, PMe_3), 26.0 (d, $^1J_{CP}$ = 35 Hz, CH_2PMe_3); $^{31}P\{^1H\}$ NMR (DMSO-d_6, 121 MHz) δ 20.1. Anal. Calcd for **7**: C, 51.3; H, 6.1; N, 11.2. Found: C, 51.0; H, 5.7; N, 11.1.

(11) Unpublished observations from this laboratory.

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