Ethylene Dimerization: An Alternative Route Involving Vinyl Hydride Intermediates

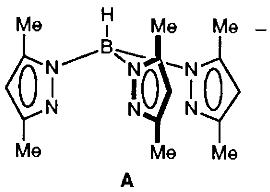
Pedro J. Pérez, Manuel L. Poveda and Ernesto Carmona*

Departamento de Química Inorgánica-Instituto de Ciencia de Materiales, Universidad de Sevilla-CSIC, Apdo. 553, 41071 Sevilla, Spain

The new complex $Tp^*Ir(C_2H_4)_2$ **1** [Tp* = hydrotris(3,5-dimethyl-1-pyrazolyl)borate] rearranges thermally into the hydrido-allyl $Tp^*Ir(H)(\eta^3\text{-}CH_2CHCHMe)$ **2** (cyclohexane, 60 °C, 15 h) through the intermediate vinyl-hydride $Tp^*Ir(H)(CH{=}CH_2)(C_2H_4)$ **3**, as demonstrated by an independent synthesis of **3** and its clean conversion into **2**.

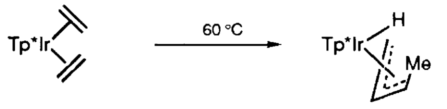
The transition metal-mediated transformations of alkenic substrates are among the most attractive and interesting processes in organometallic chemistry. Alkene dimerization has been the subject of recent and intense studies.[1] A commonly accepted mechanism for this reaction invokes the participation of a catalytically active metal-hydrido species that can undergo successive insertion of, for example, C_2H_4 to form a butyl complex.[1,2] Developments in metallacyclic chemistry have led to an alternative proposal involving metallacyclopentane intermediates,[3] while more recently, a photochemical pathway, based on binuclear vinyl species, has been advanced.[4] In this communication we present the first example of a well-defined ethylene dimerization reaction that proceeds through an isolable vinyl hydride intermediate. This transformation occurs on the iridium complex $Tp^*Ir(C_2H_4)_2$ **1** [Tp* = hydrotris(3,5-dimethyl-1-pyrazolyl)borate, structure **A**] that cleanly converts into the hydrido-allyl $Tp^*Ir(H)(\eta^3\text{-}C_4H_7)$ **2**, *via* the hydrido-vinyl $Tp^*Ir(H)(CH{=}CH_2)(C_2H_4)$ **3**.

The new complex $Tp^*Ir(C_2H_4)_2$ **1** has been prepared from $[IrCl(coe)_2]_2$ (coe = cyclooctene), ethylene and KTp*[5] following a procedure due to Oro[6] and Crabtree[7] for the unsubstituted Tp derivative. When a cyclohexane solution of **1** is heated at 60 °C for 15 h a smooth transformation ensues with formation of a new compound **2** [eqn. (1)] in *ca.* 80% isolated yield. Formulation of **2** as a hydrido-allyl species [8] comes straightforwardly from the available spectroscopic data.† Thus, a high field signal at δ −29.0 confirms the presence of a hydride ligand, while the allylic moiety, CH_2–CH–CHMe, yields characteristic signals† in the range δ 4.3–2.7, indicating trihapto coordination and an *anti* disposition of the methyl substituent. The *endo* or *exo* orientation of the allyl ligand has not been unambiguously established.



A

When the conversion of **1** into **2** is complete, NMR studies of the reaction mixture show formation of no other detectable products. However, monitoring of the reaction by ^1H NMR spectroscopy allows the observation of an intermediate species. This shows a hydride resonance‡ at δ −16.9 together with a vinylic pattern (AMX spin system, δ_A 7.38, δ_M 4.94, δ_X 5.63; $^3J_{AM}$ 18.0, $^3J_{AX}$ 10.3, $^2J_{MX}$ 2.7 Hz) suggesting formulation of the complex as $Tp^*Ir(H)(CH{=}CH_2)(C_2H_4)$, **3**. This has been confirmed by an independent high yield (80% by NMR) synthesis of **3**, achieved by the room temperature photolysis[7,9]



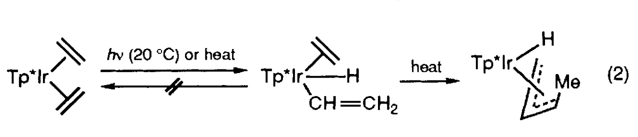
(1)

1 **2**

---

† *Selected spectroscopic data* for **2**: ^1H NMR (200 MHz, C_6D_6) δ 5.06 (dt, $^3J_{HH}$ 10.2, $^3J_{HH}$ 7.1 Hz, 1H, CH), 4.31 (quintet, $^3J_{HH}$ 6.4 Hz, 1H, C*H*Me), 3.29 (d, $^3J_{HH}$ 6.8 Hz, 1H, C*H*H), 2.74 (d, $^3J_{HH}$ 10.2 Hz, 1H, CH*H*), 1.54 (d, $^3J_{HH}$ 6.3, 3H, CH_3) and −29.0 (s, 1H, Ir-*H*); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 78.7 ($^1J_{CH}$ 161 Hz, CH), 28.7 ($^1J_{CH}$ 149 Hz, *C*HMe), 20.1 ($^1J_{CH}$ 130 Hz, CH_3) and 16.2 ($^1J_{CH}$ 158 Hz, CH_2).

‡ *Spectroscopic data* for **3**: IR (Nujol mull) 2200 cm^{-1} (ν_{Ir-H}). $^{13}C\{^1H\}$ NMR (C_6D_6) δ 126.4 ($^1J_{CH}$ 142 Hz, CH), 118.8 ($^1J_{CH}$ 151 Hz, CH_2) and 43.9 ($^1J_{CH}$ 161 Hz, C_2H_4).



1 **3** **2**

of the bis(ethylene) complex **1** [eqn. (2)]. It is interesting to point out that complex **3** transforms cleanly, and more quickly, as compared to **1**, into the allylic species **2**, no conversion being observed into the bis(alkene) derivative **1**, despite the fact that this is a very common process for most of the already known vinyl hydride complexes.[9] In fact, for unactivated alkenes, there is only one recently reported mononuclear example in which the vinylic hydride formulation is thermodynamically preferred over the alkenic isomer.[10] As in this example this thermodynamic preference may be associated with a change in the coordination mode of the Tp* ligand[10] from η^2 to η^3. The implication of vinylic species in other important transformations has been disclosed recently.[11–14]

It is noteworthy that the known compound $TpIr(C_2H_4)_2$ has been reported to decompose thermally to a complex mixture of products.[7] A similar situation holds also for the related hydrido-vinyl $TpIr(H)(CH{=}CH_2)(C_2H_4)$.[7] Hence, it seems that the presence of methyl substituents in the 3- and 5-positions of the pyrazolyl rings (or CF_3 and CH_3, as in Graham's complex[10]) not only plays a crucial role in the thermodynamic stabilization of the hydrido vinyl structure over its isomeric alkenic form, but also in the subsequent rearrangements that the hydrido vinyl species may undergo.

P. J. P. thanks the Ministerio de Educación y Ciencia for a research studentship. E. C. gratefully acknowledges financial support from the Spanish DIGICYT (project no. PB87-201), and the Junta de Andalucía. The University of Sevilla is also thanked for free access to its analytical and NMR facilities.

Received, 29th July 1991, Com. 1/03900H

References

1 G. W. Parshall, *Homogeneous Catalysis*, Wiley Interscience, New York, 1980; G. Wilke, in *Fundamental Research in Homogeneous Catalysis*, ed. M. Tsutsui, Plenum Press, New York, 1979; B. Bogdanovic, *Adv. Organomet. Chem.*, 1989, **17**, 105; S. M. Pillai, M. Ravindranathan and S. Sivaram, *Chem. Rev.*, 1986, **86**, 353; H. Yasuda and A. Nakamura, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 723.

2 B. Bogdanovic, B. Henc, H.-G. Karmann, H.-G. Nüssel, D. Walter and G. Wilke, *Ind. Eng. Chem.*, 1970, **62**, 34.

3 S. J. McLain and R. R. Schrock, *J. Am. Chem. Soc.*, 1978, **100**, 1315; S. J. McLain, J. Sancho and R. R. Schrock, *J. Am. Chem. Soc.*, 1980, **102**, 1315; R. H. Grubbs and A. Miyashita, *J. Am. Chem. Soc.*, 1978, **100**, 1300.

4 P. O. Nubel and T. L. Brown, *J. Am. Chem. Soc.*, 1984, **106**, 644.

5 S. Trofimenko, *Inorg. Synth.*, 1970, **12**, 99.

6 M. J. Fernández, M. J. Rodríguez, L. A. Oro and F. J. Lahoz, *J. Chem. Soc., Dalton Trans.*, 1989, 2073.

7 R. Tanke and R. H. Crabtree, *Inorg. Chem.*, 1989, **28**, 3444.

8 W. D. McGhee and R. G. Bergman, *J. Am. Chem. Soc.*, 1988, **110**, 4246; J.-M. Zhuang and D. Sutton, *Organometallics*, 1991, **10**, 1516 and references cited therein.

9 D. M. Haddleton and R. N. Perutz, *J. Chem. Soc., Chem. Commun.*, 1986, 1734; A. McCamley, R. N. Perutz, S. Stahl and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1690; T. W. Bell, D. M. Haddleton, A. McCamley, M. G. Partridge, R. N. Perutz and H. Willner, *J. Am. Chem. Soc.*, 1990, **112**, 9212; P. O. Stoutland and R. G. Bergman, *J. Am. Chem. Soc.*, 1988, **110**, 5732; T. T. Wenzel and R. G. Bergman, *J. Am. Chem. Soc.*, 1986, **108**, 4856; M. V. Baker and L. D. Field, *J. Am. Chem. Soc.*, 1986, **108**, 7433, 7436.

10 C. K. Ghost, J. K. Hoyano, K. Kreutz and W. A. G. Graham, *J. Am. Chem. Soc.*, 1989, **111**, 5480.

11 G. C. Bruce, S. A. R. Knox and A. Phillips, *J. Chem. Soc., Chem. Commun.*, 1990, 716.

12 J. Martínez, H. Adams, N. A. Bailey and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1989, 286; J. Martínez, J. B. Gill, H. Adams, N. A. Bailey, I. M. Saez, G. J. Sunley and P. M. Maitlis, *J. Organomet. Chem.*, 1990, **394**, 583.

13 V. C. Gibson, G. Parkin and J. E. Bercaw, *Organometallics*, 1991, **10**, 220.

14 J. W. Faller and H. Felkin, *Organometallics*, 1985, **4**, 1488.