# Iridapyrrole Complexes via Formal 3 + 2 Cycloaddition of Iridium Alkenyls to Acetonitrile

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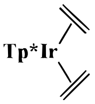
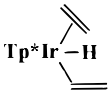
*Summary: Under appropriate conditions, the bis(ethylene) derivative* $Tp^*Ir(C_2H_4)_2$ *(Tp* = hydrotris(3,5-dimethyl-1-pyrazolyl)borate) reacts with MeCN to provide the Ir(III) complex* $Tp^*Ir(CH{=}CH_2)(C_2H_5)(NCMe)$ *(**1**). In the presence of catalytic amounts of water, **1** undergoes intramolecular coupling of the vinyl and acetonitrile ligands, with formation of a compound (**2a**) that contains a delocalized, five-membered iridapyrrole ring. This unusual cycloaddition reaction can be extended to other related alkenyl complexes of iridium.*

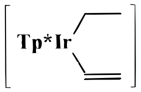
Transition-metal vinyls constitute an important group of organometallic compounds which find many applications in organic and organometallic synthesis and are also invoked as active intermediates in some catalytic processes, e.g. Fischer−Tropsch synthesis.[1,2] Recent work from this laboratory has shown that the hydridovinyl derivative $Tp^*Ir(H)(CH{=}CH_2)(C_2H_4)$ (**B**; Tp* = hydrotris(3,5-dimethyl-1-pyrazolyl)borate), which can be generated thermally or photochemically[3a] from the bis(ethylene) complex $Tp^*Ir(C_2H_4)_2$ (**A**), is capable of activating a variety of organic molecules.[3b−d] The corresponding reactions are thought to require the coordination of the organic substrate to the unsaturated iridium center **C**, which results from the insertion of $C_2H_4$ into the Ir−H bond of **B**. Prompted by these observations, we have investigated the reaction of **A** and **B** with MeCN. Nitriles are useful synthons in organic preparations[4] in addition to showing rich coordination chemistry,[5] the α-carbon exhibiting electrophilic reactivity by virtue of the contribution of the dipolar resonance structure **E**. Here we describe the unprecedented C−C coupling reaction of vinyl and acetonitrile ligands to yield iridapyrrole structures of type **F**.



**A**

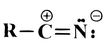


**B**

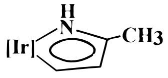


**C**

**D**



**E**



**F**

Upon heating of acetonitrile solutions of **A** or **B** to 60 °C, a smooth reaction ensues that results in the new complex **1** in essentially quantitative yield (Scheme 1). Identification of **1** is straightforward on the basis of its spectroscopic properties,[6] which are very similar to those of the Rh analogue.[7] Further heating of the colorless solutions of **1** to 100 °C produces a pale red solution that affords, after workup, the crystalline material **2a**, which has the same analytical composition as **1**. Spectroscopic

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(1) (a) Turner, M. L.; Byers, P. K.; Long, H. C.; Maitlis, P. J. *J. Am. Chem. Soc.* **1993**, *115*, 4417. (b) Martínez, J.; Gill, J. B.; Adams, H.; Bailey, N. A.; Saez, I. M.; Sunley, G. J.; Maitlis, P. M. *J. Organomet. Chem.* **1990**, *394*, 583. (c) Braun, T.; Gevert, O.; Werner, H. *J. Am. Chem. Soc.* **1995**, *117*, 7291. (d) Schäfer, M.; Mahr, N.; Wolf, J.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1315. (e) Selnau, H. E.; Merola, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 4008.

(2) (a) Gibson, V. C.; Parkin, G.; Bercaw, J. E. *Organometallics* **1991**, *10*, 220. (b) Belderraín, T. R.; Nicasio, M. C.; Paneque, M.; Poveda, M. L.; Carmona, E. *Gazz. Chim. Ital.* **1994**, *124*, 341.

(3) (a) Pérez, P. J.; Poveda, M. L.; Carmona, E. *J. Chem. Soc., Chem. Commun.* **1992**, 8. (b) Boutry, O.; Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Pérez, P. J.; Carmona, E. *J. Am. Chem. Soc.* **1992**, *114*, 7288. (c) Gutiérrez, E.; Monge, A.; Nicasio, M. C.; Poveda, M. L.; Carmona, E. *J. Am. Chem. Soc.* **1994**, *116*, 791. (d) Paneque, M.; Poveda, M. L.; Rey, L.; Taboada, S.; Carmona, E. *J. Organomet. Chem.* **1995**, *504*, 147.

(4) (a) Bianchini, C.; Meli, A.; Peruzzini, M.; Vacca, A.; Vizza, F. *Organometallics* **1991**, *10*, 645. (b) Erker, G.; Kowalski, D.; Noe, R.; Krüger, C.; Nolte, M. *Tetrahedron Lett.* **1994**, *35*, 6665. (c) Erker, G.; Pfaff, R. *Organometallics* **1993**, *12*, 1921.

(5) See for example: (a) Feng, S. G.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 8613. (b) Feng, S. G.; White, P. S.; Templeton, J. L. *Organometallics* **1994**, *13*, 1214. (c) Endres, H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Guillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1987; Vol. II, Chapter 13.7.

(6) Satisfactory analytical data for all new compounds have been obtained. (a) Compound **A** (0.2 g, ca. 0.36 mmol) was dissolved in neat acetonitrile (20 mL), and the solution was heated overnight to 60 °C. Removal of the solvent in vacuo left a white residue of analytically pure **1**, which was recrystallized from MeCN. Selected NMR data: $^1H$ (300 MHz, $CDCl_3$) AMX spin system, $\delta_A$ 8.24, $\delta_M$ 5.55, $\delta_X$ 4.73 ($^3J_{AM}$ = 10, $^3J_{AX}$ = 18, $^2J_{MX}$ = 4 Hz) for $Ir{-}CH_A{=}CH_MH_X$, 2.12 (m, 1 H, Ir−C*H*H), 1.9 (m, 1H, Ir−CH*H*), 0.43 (t, 3H, $IrCH_2CH_3$); $^{13}C\{^1H\}$ (75 MHz, $CDCl_3$) 138.3 (Ir−*C*H=CH₂), 114.2 (Ir−CH=*C*H₂), 3.9 (Ir−NC*C*H₃), −11.9 (Ir−*C*H₂CH₃). Anal. Calcd for $BC_{21}H_{33}IrN_7$: C, 43.00; H, 5.67; H, 16.72. Found: C, 43.58; H, 5.65; N, 15.02. (b) The iridapyrrole derivative **2a** formed in essentially quantitative yield when solutions of **1** in acetonitrile, to which 1−2 drops of water had been added, were heated to 100 °C in a sealed ampule. Selected spectroscopic data (see **G** or **H** for assignment): $^1H$ NMR (300 MHz, $CDCl_3$) δ 10.71 (d, $H^1$, $^3J_{HH}$ = 7 Hz), 8.18 (br s, $H^3$), 6.82 (dd, $H^2$, $^4J_{HH}$ = 3 Hz), 1.23, 1.12 (dq, 1 H each, $^2J_{HH}$ = 11, $^3J_{HH}$ = 8 Hz, Ir-C*H*₂CH₃), 0.06 ppm (t, 3H, $IrCH_2CH_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 191.3 ($C^1$), 181.8 ($C^3$), 131.3 ($C^2$), −16.9 (Ir−*C*H₂CH₃). Anal. Calcd for $BC_{21}H_{33}IrN_7$: C, 43.00; H, 5.67; H, 16.72. Found: C, 43.03; H, 5.65; N, 16.74. (c) Selected spectroscopic data for **2c**: $^1H$ NMR (300 MHz, $CDCl_3$) δ 10.07 (d, $H^1$, $^3J_{HH}$ = 7 Hz), 7.9 (br s, $H^3$), 6.92 (dd, $H^2$, $^4J_{HH}$ = 3 Hz), 1.17, 1.04 (dq, 1 H each, $^2J_{HH}$ = 11, $^3J_{HH}$ = 8 Hz, Ir−C*H*₂CH₃), 0.54 ppm (t, 3H, $IrCH_2CH_3$); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 194.0 ($C^1$), 187.0 ($C^3$), 131.1 ($C^2$), −11.5 (Ir−*C*H₂CH₃). Selected spectroscopic data for **2d**: $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 198.6 ($C^1$), 184.1 ($C^3$), 140.0 ($C^2$), 2.5 (Ir−*C*H(cyclooctyl)). Anal. Calcd for $BC_{27}H_{41}IrN_7$: C, 48.64; H, 6.20; H, 14.71. Found: C, 49.04; H, 6.69; N, 14.23.

(7) Pérez, P. J.; Poveda, M. L.; Carmona, E. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 231.

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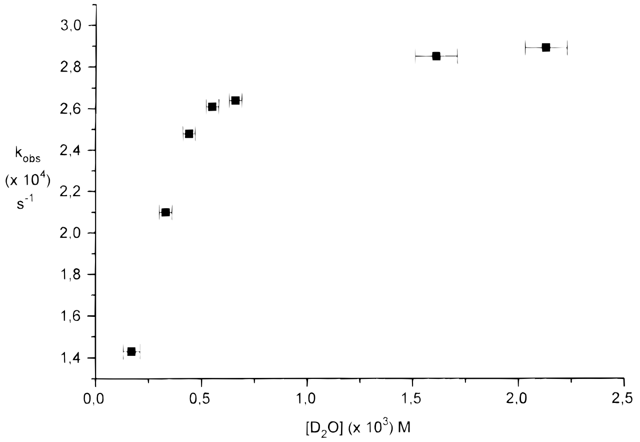
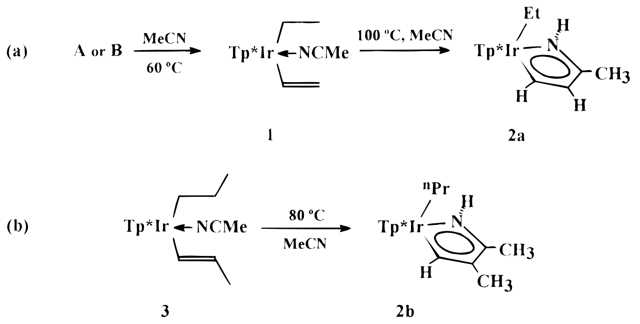
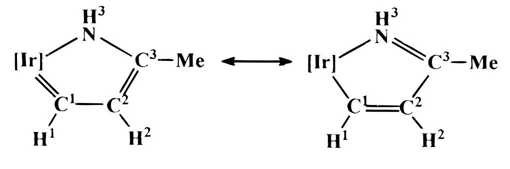


**Figure 1.** $k_{obs}$ vs [$D_2O$] representation for the conversion **1** to **2a**.

**Scheme 1**



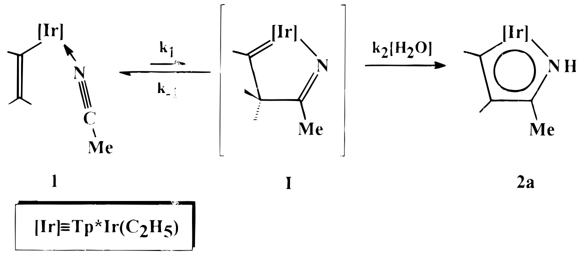
data, including multinuclear 1D and 2D NMR experiments, are consistent with the delocalized iridapyrrole structure shown in Scheme 1 (see canonical forms **G** and **H**). For example, the iridium-bonded methine unit ($C^1$—$H^1$) is responsible for resonances at $\delta$ 10.71 and 191.3 in the $^1H$ and $^{13}C\{^1H\}$ NMR spectra, respectively. These signals are clearly in a range intermediate between those of metal—carbene and metal—vinyl resonances.[8] Additional support for the proposed aromaticity of **2a** is provided by the 3 Hz value found for the four-bond $H^2$—$H^3$ coupling constant.



G                    H

Preliminary kinetic and mechanistic studies shed some light on the course of this coupling reaction, the following pieces of information being particularly worthy of note. (a) The process is catalyzed by water; a graphical representation of $k_{obs}$ vs [$D_2O$] shows saturation kinetics (Figure 1). (b) It is intramolecular, exhibiting pseudo-first-order behavior with relatively little incorporation (<15%) of $CD_3CN$ being observed when **1** is heated in neat $CD_3CN$ under saturation conditions.

**Scheme 2**



(c) The analogous reaction of the propenyl complex **3**[9] shows remarkable selectivity (Scheme 1, reaction b), yielding compound **2b** as the only detectable product.

The above observations would not appear to be a simple insertion reaction, i.e. a formal 1,3-vinyl shift from the metal to the α-carbon of the nitrile, as has been proposed for complexes of the early transition metals.[10] Instead, they point to a direct coupling of the Ir—CH=$CH_2$ fragment with the coordinated molecule of acetonitrile, to generate the undetected iridacycle **I** (Scheme 2), subsequently trapped as the thermodynamically favored iridapyrrole **2a** by a water-dependent tautomerism process.[11] The rate expression for such a mechanism is given in eq 1; $k_1$ and $k_{-1}/k_2$ values of

$$\text{rate} = k_{\text{obs}}[\mathbf{1}] = \frac{k_1 k_2[D_2O]}{k_{-1} + k_2[D_2O]} \tag{1}$$

[3.2(2)] × $10^{-4}$ $s^{-1}$ and 0.16(4) M, respectively, can be computed from the data of Figure 1. It should be emphasized that as a result of the experimental method the above figures are subject to significant uncertainty, particularly $k_{-1}/k_2$.

Further support for the proposed mechanism comes from the measurement of an inverse deuterium kinetic isotope effect (KIE) in the saturation regime when using $Tp^*Ir(C_2D_3)(C_2D_5)(NCMe)$, **1-d₈** ($k^H_{obs}/k^D_{obs}$ = 0.87(2), [$D_2O$] = 2.1(1) M). This measurement not only shows that no significant C—H bond breaking occurs in the transition state of the rate-determining step but also constitutes additional support for the $sp^2$-to-$sp^3$ change in hybridization at the nucleophilic $\beta$-vinyl carbon as implied by this mechanism.[12a,b] Inverse KIE's have been reported for reactions involving hydrogen atom transfer, most notably in the reductive elimination of alkanes from $\sigma$-alkyl metal hydrides,[12c–f] and have been interpreted as evidence for the existence of a preequilibrium between M(R)H and an unobserved metal—alkane $\sigma$-complex.

Attracted by this unusual reactivity of the Ir—vinyl fragments toward MeCN,[13] we have sought its gener-

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(8) (a) Bleeke, J. R.; Ortwerth, M. F.; Rohde, A. M. *Organometallics* **1995**, *14*, 2813. (b) Bleeke, J. R.; Ortwerth, M. F.; Chiang, M. Y. *Organometallics* **1992**, *11*, 2740. (c) DeShong, P.; Sidler, D. R.; Rybczynski, P. J.; Slough, G. A.; Rheingold, A. *J. Am. Chem. Soc.* **1988**, *110*, 2575. (d) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199.

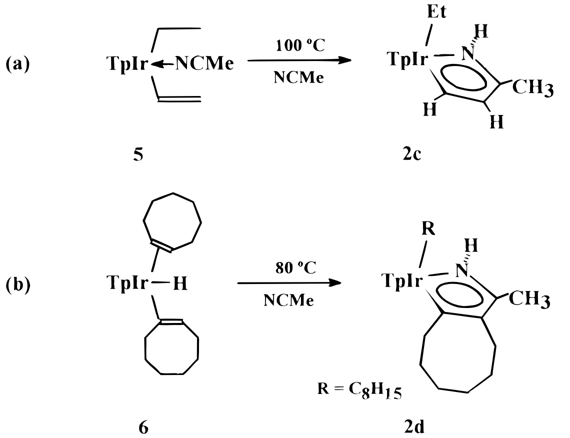
(9) This compound was obtained by following a procedure similar to that described above for **1**.

(10) See for example: (a) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443. (b) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Organometallics* **1988**, *7*, 1148. (c) Doxsee, K. M.; Mouser, J. K. M. *Organometallics.* **1990**, *9*, 3012. (d) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325.

(11) The mechanism of this isomerization has not been investigated.

(12) (a) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*; Harper and Row: New York, 1987; Chapter 2. (b) Lee, Y. *Chem. Soc. Rev.* **1995**, 223. (c) Bullock, R. M.; Headford, C. E. L.; Hennessy, K. M.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 3897. (d) Buchanan, J. M.; Stryker, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 1537. (e) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332–7346. (f) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346–7355.

**Scheme 3**



alization to other related systems. Preliminary results indicate benzonitrile behaves similarly. Moreover, complexes of the unsubstituted Tp ligand[14] originating from both simple olefins such as ethylene[15] and internal olefins such as cyclooctene readily take part in this transformation (Scheme 3).

The generation of the iridapyrrole **2a** in the described process can be viewed as a formal [3 + 2] cycloaddition of nitrile and metal−vinyl fragments, with the formation of the aromatic heterometallacycle providing the driving force for the reaction. Alternatively, if the canonical form Ir$^+$=CH−CH$_2^-$ [16] has an important contribution to the electronic structure of the Ir−vinyl moiety, the above transformation could be regarded as a 1,3-dipolar cycloaddition, a reaction not very commonly encountered in organometallic chemistry.[17] The formation of metallapyrrole derivatives, albeit by different synthetic methodologies, is not unprecedented in the literature.[18] Notwithstanding and irrespective of its intimate mechanism, the C−C coupling of the $\beta$-vinyl carbon and the acetonitrile ligand reported in this contribution documents a new kind of reactivity of metal−vinyl fragments.[19]

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[13] The participation of the nitrile C−N multiple bond in organometallic reactions is relatively uncommon, although there are precedents in the literature. See for example: (a) Beckhaus, R.; Strauss, I.; Wagner, T. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 688. (b) Cohen, S. A.; Bercaw, J. E. *Organometallics.* **1985**, *4*, 1006. (c) Doxsee, K. M.; Farahi, J. B.; Hope, H. *J. Am. Chem. Soc.* **1991**, *113*, 8889. See also ref 10a,c. For pyridine synthesis involving formal coupling of two alkynes and nitriles: (d) Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 248. (e) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 2211.

[14] (a) Fernández, M. J.; Rodríguez, M. J.; Oro, L. A.; Lahoz, F. J. *J. Chem. Soc., Dalton Trans.* **1989**, 2073. (b) Tanke, R.; Crabtree, R. H. *Inorg. Chem.* **1989**, *28*, 3444.

[15] The complex TpIr($C_2H_3$)($C_2H_5$)(NCMe) can also be prepared from the corresponding bis(ethylene) derivative[14] using a procedure similar to that already described for the Tp* analog **1**.

[16] Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. G.; Georgion, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688 and references cited therein.

[17] (a) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1077. (b) Fermin, M. C.; Bruno, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 7511. (c) Chetcuti, P. A.; Walker, J. A.; Knobler, C. B.; Hawthorne, M. F. *Organometallics* **1988**, *7*, 641. (d) de Lange, P. P. M.; van Wijnkoop, M.; Frühauuf, H.-W.; Vrieze, K.; Goubitz, K. *Organometallics* **1993**, *12*, 428.

[18] (a) Werner, H.; Daniel, T.; Braun, T.; Nürnberg, O. *J. Organomet. Chem.* **1994**, *480*, 145. (b) Martin, G. C.; Boncella, J. M.; Wucherer, E. J. *Organometallics* **1991**, *10*, 2804. (c) Filippou, A. C.; Völkl, C.; Kiprof, P. *J. Organomet. Chem.* **1991**, *415*, 375. (d) Guram, A. S.; Jordan, R. F. *J. Org. Chem.* **1993**, *58*, 5595. For a highly distorted structure see: Curtis, M. D.; Real, J.; Hirpo, W.; Butler, W. H. *Organometallics* **1990**, *9*, 66.

[19] The closest proposed reactions we are aware of involve (a) the C−C coupling of the terminal =CH$_2$ of vinylimido complexes[13b,c] or $\eta^1$-allyls (Klei, E.; Teuben, J. H.; de Liefde Meijer, H. J.; Kwak, E. J.; Bruins, A. P. *J. Organomet. Chem.* **1982**, *224*, 327) and (b) the C−X coupling of $\eta^1$-iminoacyls (X = N[17a]) and $\eta^1$-ketene complexes (X = O[17b]). Although nitrile precoordination was suggested in some of these reactions, in no case was the simple adduct detected.