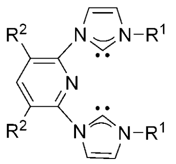
DOI: 10.1002/anie.200804573

"Pincer" Pyridine–Dicarbene–Iridium Complexes: Facile C–H Activation and Unexpected η^2-Imidazol-2-ylidene Coordination**

Andreas A. Danopoulos, David Pugh, and Joseph A. Wright*

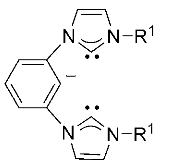
Anionic 2,6-diphosphinomethylphenyl (P–C–P), 2,6-diphosphinitophenyl (PO–C–OP), and neutral 2,6-diphosphinomethylpyridine (P–N–P) "pincer" complexes of iridium have been studied as catalysts in important organometallic transformations, including alkane dehydrogenation (in the presence or absence of an H_2 acceptor), dehydrogenation of primary amines to nitriles, and dehydrogenation of borane–amine complexes.[1] Furthermore, interesting stoichiometric, intermolecular C-H activations of substituted aromatic compounds (anisole, acetophenone, and halobenzenes) have been realized.[2] This remarkable reactivity is, in part, due to the thermal stability and rigidity that the "pincer" imparts on the Ir center, although reports of ligand "non-innocence" have appeared.[3] Intramolecular metalations of ligand C–H bonds are known in [Ir(P–C–P)] complexes.[4] Owing to the relevance of these catalytic transformations to the atom- and energy-efficient use of organic molecules, the further development of new Ir "pincer" complexes with improved activity and selectivity is a goal of much current research.

To this end, we considered the replacement of the P donors of the "pincer" arms by N-heterocyclic carbenes (NHCs, see below), which, based on the accepted analogy between trialkylphosphine and N-heterocyclic carbene (NHC) ligands,[5] would result in novel highly reactive complexes.



C_{NHC}-N-C_{NHC}: R^1 = alkyl or aryl, R^2 = H

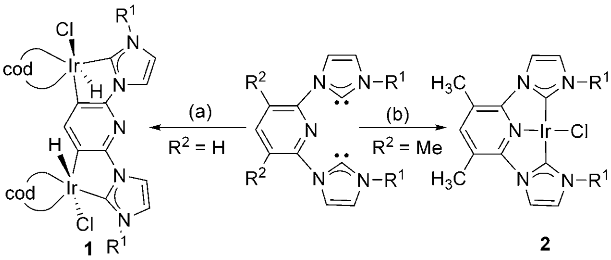
C_{NHC}-N^{Me}-C_{NHC}: R^1 = alkyl or aryl, R^2 = Me



C_{NHC}-C-C_{NHC}: R^1 = alkyl or aryl, R^2 = H

Even though complexes of the ligands 2,6-bis(imidazol-2-ylidene)phenyl (C_{NHC}–C–$C_{NHC)}$ and 2,6-bis(imidazol-2-ylidene)pyridine (C_{NHC}–N–C_{NHC}) are known with many metals,[6] such iridium complexes are very rare. Reactions of the bis-imidazolium salt (CH_{NHC}–CH–CH_{NHC})X_2 ($X = I^-$) with the iridium precursors [{Ir(cod)Cl}$_2$] or [{Ir(coe)$_2$Cl}$_2$] (cod = 1,5-cyclooctadiene, coe = cyclooctene), in the presence of Et_3N or [Zr(NMe$_2$)$_4$], led to [Ir^{III}(C_{NHC}-C-C_{NHC})I_2]. Kinetically stable bimetallic Ir^{III} species were formed in competition with the mononuclear complex.[7,8]

A careful study of the reaction of [{Ir(cod)Cl}$_2$] with C_{NHC}–N–C_{NHC} at lower temperatures (−78 to −30 °C) led to the isolation of **1**, which was unstable above −30 °C and was crystallized at −50 °C (Scheme 1). The quality of the X-ray data for **1** collected at low temperatures was only enough to show the connectivity of the non-hydrogen atoms. The proposed structure, with *trans* hydrides, was also based on mechanistic considerations and analogous stable mononuclear pyridyl–NHC complexes.[9] Pyridine metalation was prevented by using the C_{NHC}–N^{Me}–C_{NHC} ligand, with a modified backbone, methylated at the 3- and 5-positions of the pyridine ring. Reaction of C_{NHC}–N^{Me}–C_{NHC}[10] with [{Ir(coe)$_2$Cl}$_2$] gave the green, air-sensitive complex [Ir(C_{NHC}–N^{Me}–C_{NHC})Cl] (**2**).



Scheme 1. Synthesis of complexes **1** and **2**. Reagents:a) [{Ir(cod)Cl}$_2$], THF, −78 to −30 °C; b) [{Ir(coe)$_2$Cl}$_2$], THF, −78 °C to room temperature. R^1 = 2,6-diisopropylphenyl.

Substitution of Cl^- in **2** by neutral donors led to the isolation of **3** and **4** in high yields (Scheme 2). The CO stretching frequency ($\nu = 1980\ cm^{-1}$) indicated that the cationic Ir^I center in **3c** is a weaker π donor to CO than in [Ir(P–N–P)(CO)]$^+$ ($\nu = 1962\ cm^{-1}$).[11] As anticipated, the neutral Ir^I center in [Ir(P–C–P)(CO)] and [Ir(PO–C–OP)(CO)] are also stronger π donors [ν(CO) = 1913 and 1949 cm^{-1}, respectively].[1f]

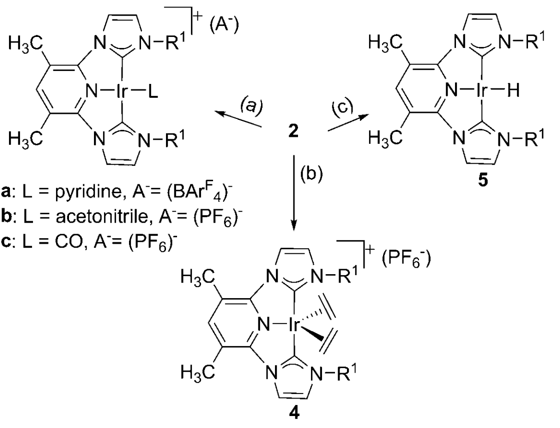
Single-crystal X-ray diffraction studies revealed that complex **4** (Figure 1) adopted a distorted trigonal bipyramidal geometry. The axes of the coordinated ethylene groups are parallel, reminiscent of the conformation seen in the [Ir(PR$_3$)$_3$(C_2H_4)$_2$]$^+$ (PR$_3$ = trialkylphosphine).[12] The Ir–C_{NHC} and Ir–$C_{ethylene}$ bond lengths agree with literature data.[13]

---

[*] Dr. A. A. Danopoulos, Dr. D. Pugh, Dr. J. A. Wright
School of Chemistry, University of Southampton
Highfield, Southampton, SO17 1BJ (UK)
Fax: (+44) 2380-596-805
E-mail: ad1@soton.ac.uk

[**] We are grateful to Prof. W. Clegg at the EPSRC single crystal synchrotron service at Daresbury[18] for the data collection of complexes **4** and **6**, and Johnson-Matthey for a loan of iridium salts.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200804573.



3a: L = pyridine, A⁻= $(BAr^F{}_4)^-$
3b: L = acetonitrile, A⁻= $(PF_6)^-$
3c: L = CO, A⁻= $(PF_6)^-$

Scheme 2. Reagents: a) $NaBAr^F{}_4$ [Ar^F = 3,5-bis-(trifluoromethyl)phenyl], pyridine (**3a**)/KPF_6, MeCN (**3b**)/KPF_6, CO (**3c**); b) KPF_6, $CH_2{=}CH_2$; c) NaO*i*Pr, THF.

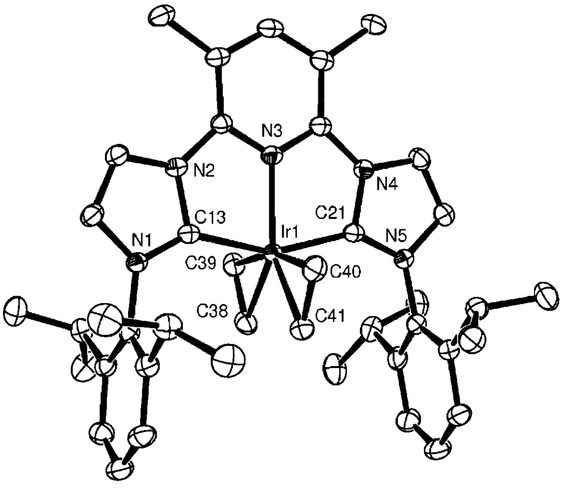


Figure 1. ORTEP representation of the cation in **4**. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Ir1–C13 2.019(3), Ir1–C21 2.018(3) C38–C39 1.439(5) C40–C41 1.422(4).

Bis(ethylene) complexes are not known for the related [Ir(P–N–P)] system.

Substitution of the chloride ion in **2** by NaO*i*Pr gave the mononuclear Ir^I hydride **5** after elimination of acetone (Scheme 2, Figure 2).[14] The presence of an Ir–H species was established by ^1H NMR and IR spectroscopy. Complex **5** is a rare example of an Ir^I hydride with NHC donors. The study of its reactivity with small molecules is currently underway, and will be reported in a full paper.

During the synthesis of **2**, minor amounts of an orange complex were obtained, especially if the reaction was carried out at room temperature. This complex could be separated from **2**, because of its low solubility in diethyl ether, and was crystallized after anion exchange (with KPF_6) to give **6** (Figures 3 and 4), a bimetallic PF_6^- salt, containing one Ir^I center and one Ir^{III} center.

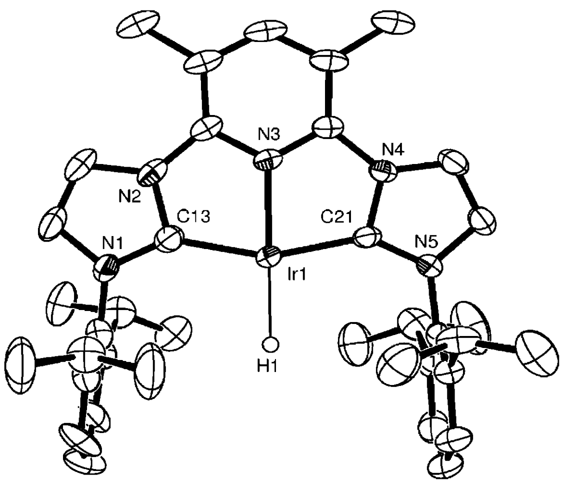


Figure 2. ORTEP representation of **5**. Thermal ellipsoids are set at 50% probability. Hydrogen atoms (with the exception of H1) are omitted for clarity. Selected bond lengths [Å]: C13–Ir1 1.972(4) C21–Ir1 1.964(4).

The Ir^{III} center (crystallographic Ir1) is coordinated to two NHCs of a C_{NHC}–N^{Me}–C_{NHC} pincer ligand, one chloride, and one η^3-allyl group, which originated from metalation of one *o*-*i*Pr substituent of the NHC ligand.[15] The coordination sphere of Ir^I (crystallographic Ir2) comprises one C_{NHC}–N^{Me}–C_{NHC} "pincer" which is bound with one normal and one abnormal NHC,[16] one chloride, and one NHC that is bound in a η^2-ethylene-like fashion, from the unsaturated backbone of the imidazol-2-ylidene, forming a bridge between the Ir^I and Ir^{III} centers.

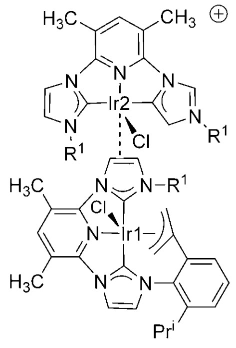


Figure 3. Diagram of **6**.

To our knowledge, this NHC bonding mode is unprecedented and has the following structural implications: 1) Elongation of the backbone C=C bond of the η^2-coordinated NHC [1.460(4) Å, as compared with 1.336(4) Å in C_{NHC}–N^{Me}–

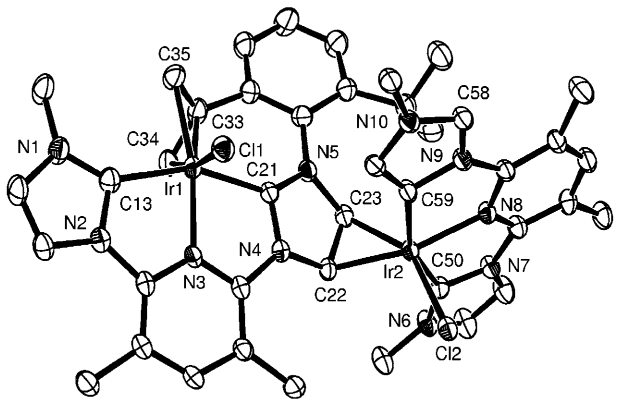


Figure 4. ORTEP representation of the cation in **6**. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity. Only the *ipso* carbon of the aromatic substituents attached at N1, N6, and N10 is shown. Selected bond lengths [Å]: C13–Ir1 2.065(3) C21–Ir1 2.015(3) C50–Ir2 2.002(3) C59–Ir2 2.033(3) C22–C23 1.460(4).

C_{NHC},[10] 1.331(5)–1.336(5) Å in various Ir^{I} and Ir^{III} NHC complexes,[7,13] and 1.422(4)–1.439(5) Å in the η^2 ethylenes of **4**]; 2) an increase in the N-C_{NHC}-N bond angle [107.7(3)°, as compared to 101.7(2)° in the NHC of the free C_{NHC}–N^{Me}–C_{NHC} and 103.7(3)° in the NHC coordinated to Ir]; 3) shortening of the Ir1−C_{NHC} bond length in the η^2-bound NHC ligand [Ir1-C_{NHC} = 2.015(3) Å, as compared to 2.065(3) Å in the normally bound NHC ligand]. The latter may suggest that the perturbation of the NHC aromaticity on η^2 coordination strengthens the Ir−C_{NHC} bond, in analogy to cyclic saturated or acyclic nucleophilic carbene ligands.[17]

In summary, we have prepared a series of [Ir^{I}(C_{NHC}–N^{Me}–C_{NHC})] complexes by suitable ligand tuning. A sequence of facile metalations of sterically accessible C−H bonds (*i*Pr and abnormal NHC) testifies to the reactivity of the iridium center. A unique η^2-NHC bonding was also detected. The realization of η^2-NHC bonding may initiate efforts to use NHCs as homo- or heterometallic bridging ligands, giving rise to novel materials or catalytic complexes. It may also be the initial step in the imidazol-2-ylidene ring-opening or render unsaturated imidazol-2-ylidenes as catalyst poisons in certain NHC-catalyzed reactions.

Future work is aimed at studying the catalytic reactivity of **2**–**5**, designing "spectator" pincer NHC ligands, and exploring the scope of the novel η^2-NHC coordination in homogeneous catalysis by NHC complexes.

Experimental Section

2: A solution of C_{NHC}–N^{Me}–C_{NHC} (200 mg, 0.36 mmol) in THF (10 mL) at −78 °C was added to a solution of [{IrCl(coe)$_2$}$_2$] (95 mg) in THF (10 mL) at −78 °C, stirred for 15 mins, warmed to room temperature and stirred for 12 h. Volatiles were removed under reduced pressure The green-brown solid residue was washed with light petroleum (2 × 15 mL), and extracted into diethyl ether (3 × 20 mL). Evaporation of the diethyl ether extracts afforded **2** as a a green solid (150 mg, 53 %).

6: The diethyl ether insoluble residue (see above) was dissolved in THF (5 mL) and, after addition of KPF_6 (30 mg), the mixture was stirred for 24 h. The crude product was isolated by filtration of KCl and evaporation of the volatiles under vacuum. Crystallization from THF/diethyl ether afforded **6** as orange plates.(ca. 20 mg, ca. 7 %).

Crystal data: CCDC 702016 (**4**), CCDC 702017 (**5**), and CCDC 702018 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4:[18] $C_{41}H_{53}F_6IrN_5P$, $M_r = 953.05$, triclinic, space group $P\bar{1}$, $a = 8.5051(6)$, $b = 15.1440(4)$, $c = 16.5098(5)$ Å, $\alpha = 105.8720(10)$, $\beta = 101.4970(2)$, $\gamma = 91.0240(10)°$; $V = 1998.5(2)$ Å^3, $T = 120(2)$ K, $Z = 2$; 21 458 reflections measured, 11 584 unique ($R_{int} = 0.0420$), which were used in all calculations. The final $wR(F^2)$ was 0.0864 (all data) and $R = 0.0334$ [$I > 2\sigma(I)$].

5: $C_{37}H_{46}IrN_5$, $M_r = 752.99$, triclinic, space group $P\bar{1}$, $a = 11.7002(4)$, $b = 12.2554(4)$, $c = 12.7077(5)$ Å, $\alpha = 83.460(2)$, $\beta = 80.693(2)$, $\gamma = 71.350(2)°$; $V = 1699.98(10)$ Å^3, $T = 120(2)$ K, $Z = 2$; 31 429 reflections measured, 7776 unique ($R_{int} = 0.0410$), which were used in all calculations. The final $wR(F^2)$ was 0.0736 (all data) and $R = 0.0358$ [$I > 2\sigma(I)$].

6:[18] $C_{80}H_{99}Cl_2F_6Ir_2N_{10}O_2P$; $M_r = 1832.96$, triclinic, space group $P\bar{1}$, $a = 16.618(5)$, $b = 17.523(5)$, $c = 18.315(5)$ Å, $\alpha = 65.338(3)$, $\beta = 70.541(3)$, $\gamma = 66.844(3)°$; $V = 4364(2)$ Å^3, $T = 120(2)$ K, $Z = 2$; 41 356 reflections measured, 21 172 unique ($R_{int} = 0.0298$), which were used in all calculations. The final $wR(F^2)$ was 0.0830 (all data) and $R = 0.0322$ [$I > 2\sigma(I)$].

Received: September 17, 2008

Keywords: C−H activation · carbenes · hydrides · iridium · nitrogen heterocycles

---

[1] For leading references see: a) C. M. Jensen, *Chem. Commun.* **1999**, 2443; b) C. M. Jensen, M. Brookhart, *Science* **2006**, *312*, 257; c) M. E. van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759; d) K. Krogh-Jespersen, M. Czerw, N. Summa, K. B. Renkema, P. D. Achord, A. S. Goldman, *J. Am. Chem. Soc.* **2002**, *124*, 11404; e) I. Göttker-Schnetmann, P. S. White, M. Brookhart, *Organometallics* **2004**, *23*, 1776; f) W. H. Bernskoetter, M. Brookhart, *Organometallics* **2008**, *27*, 2036; g) M. C. Denney, V. Pons, T. J. Hebden, D. M. Heinekey, K. I. Goldberg, *J. Am. Chem. Soc.* **2006**, *128*, 12048.

[2] a) M. Feller, A. Karton, G. Leitus, J. M. L. Martin, D. Milstein, *J. Am. Chem. Soc.* **2006**, *128*, 12400; b) E. Ben-Ari, R. Cohen, M. Gandelman, L. J. W. Shimon, J. M. L. Martin, D. Milstein, *Organometallics* **2006**, *25*, 3190.

[3] E. Ben-Ari, G. Leitus, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.* **2006**, *128*, 15390.

[4] H. A. Y. Mohammad, J. C. Grimm, K. Eichele, H.-G. Mack, B. Speiser, F. Novak, M. G. Quintanilla, W. C. Kaska, H. A. Mayer, *Organometallics* **2002**, *21*, 5775.

[5] J. C. Green, B. J. Herbert, *Dalton Trans.* **2005**, 1214.

[6] D. Pugh, A. A. Danopoulos, *Coord. Chem. Rev.* **2007**, *251*, 610.

[7] a) E. B. Bauer, G. T. S. Andavan, T. K. Hollis, R. J. Rubio, J. Cho, G. R. Kuchenbeiser, T. R. Helgert, C. S. Letko, F. S. Tham, *Org. Lett.* **2008**, *10*, 1175; b) M. Raynal, C. S. J. Cazin, C. Vallée, H. Olivier-Bourbigou, P. Braunstein, *Chem. Commun.* **2008**, 3983.

[8] J. A. Wright, A. A. Danopoulos, W. B. Motherwell, R. J. Carroll, S. Ellwood, J. Saßmannshausen, *Eur. J. Inorg. Chem.* **2006**, 4857.

[9] A. A. Danopoulos, M. B. Hursthouse, S. Winston, *J. Chem. Soc. Dalton Trans.* **2002**, 3090.

[10] D. Pugh, A. Boyle, A. A. Danopoulos, *Dalton Trans.* **2008**, 1087.

[11] S. M. Kloek, D. M. Heinekey, K. I. Goldberg, *Organometallics* **2006**, *25*, 3007.

[12] E. G. Lundquist, K. Folting, W. E. Streib, J. C. Huffman, O. Eisenstein, K. G. Caulton, *J. Am. Chem. Soc.* **1990**, *112*, 855.

[13] N. Stylianides, A. A. Danopoulos, N. Tsoureas, *J. Organomet. Chem.* **2005**, *690*, 5948.

[14] J. Zhao, H. Hesslink, J. F. Hartwig, *J. Am. Chem. Soc.* **2001**, *123*, 7220.

[15] a) For H/D exchange and single metalation of the *o*-*i*Pr substituents see: W. H. Bernskoetter, E. Lobkovsky, P. J. Chirik, *Organometallics* **2005**, *24*, 4367; b) for C−H activation of alkyl and aryl substituents of [Ir(NHC)] complexes see: M. Viciano, M. Feliz, R. Corberan, J. A. Mata, E. Clot, E. Peris, *Organometallics* **2007**, *26*, 5304; c) for C−H activation on two *tert*-butyl substituents of a NHC ligand coordinated to Ir, see: N. M. Scott, R. Dorta, E. D. Stevens, A. Correa, L. Cavallo, S. P. Nolan, *J. Am. Chem. Soc.* **2005**, *127*, 3516.

[16] A. R. Chianese, A. Kovacevic, B. M. Zeglis, J. W. Faller, R. H. Crabtree, *Organometallics* **2004**, *23*, 2461.

[17] Y. Canac, M. Soleilhavoup, S. Conejero, G. Bertrand, *J. Organomet. Chem.* **2004**, *689*, 3857.

[18] R. J. Cernik, W. Clegg, C. R. A. Catlow, G. Bushnell-Wye, J. V. Flaherty, G. N. Greaves, M. Hamichi, I. Burrows, D. J. Taylor, S. J. Teat, *J. Synchrotron Radiat.* **1997**, *4*, 279.