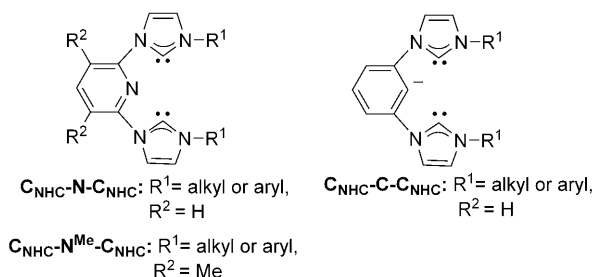


“Pincer” Pyridine–Dicarbene–Iridium Complexes: Facile C–H Activation and Unexpected η^2 -Imidazol-2-ylidene Coordination**

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.

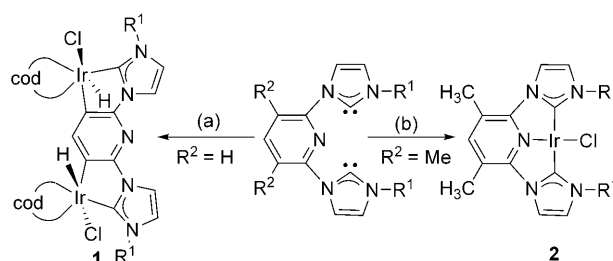
To this end, we considered the replacement of the P donors of the “pincer” arms by N-heterocyclic carbenes (NHCs, see below), which, based on the accepted analogy between trialkylphosphine and N-heterocyclic carbene (NHC) ligands,^[5] would result in novel highly reactive complexes.



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 $[Ir(coe)_2Cl]_2$ ($cod = 1,5$ -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 $-30^\circ C$) led to the isolation of **1**, which was unstable above $-30^\circ C$ and was crystallized at $-50^\circ C$ (Scheme 1). The quality of the X-ray



Scheme 1. Synthesis of complexes **1** and **2**. Reagents: a) $[Ir(cod)Cl]_2$, THF, -78 to $-30^\circ C$; b) $[Ir(coe)_2Cl]_2$, THF, $-78^\circ C$ to room temperature. R^1 = 2,6-diisopropylphenyl.

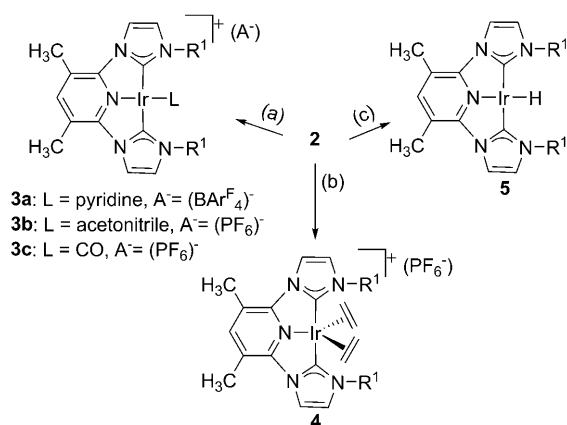
data for **1** collected at low temperatures was only enough to show the connectivity of the non-hydrogen atoms. The proposed structure, with *trans* hydrides, was also based on mechanistic considerations and analogous stable mononuclear pyridyl–NHC complexes.^[9] Pyridine metalation was prevented by 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 $[Ir-(coe)_2Cl]_2$ gave the green, air-sensitive complex $[Ir(C_{NHC}-N^{Me}-C_{NHC})Cl]$ (**2**).

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 ($\nu = 1980\text{ cm}^{-1}$) indicated that the cationic Ir^I center in **3c** is a weaker π donor to CO than in $[Ir(P-N-P)(CO)]^+$ ($\nu = 1962\text{ cm}^{-1}$).^[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 [$\nu(CO) = 1913$ and 1949 cm^{-1} , respectively].^[14]

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]

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Scheme 2. Reagents: a) NaBARF₄ [Ar^F = 3,5-bis-(trifluoromethyl)phenyl], pyridine (**3a**)/KPF₆, MeCN (**3b**)/KPF₆, CO (**3c**); b) KPF₆, CH₂=CH₂; c) NaOiPr, THF.

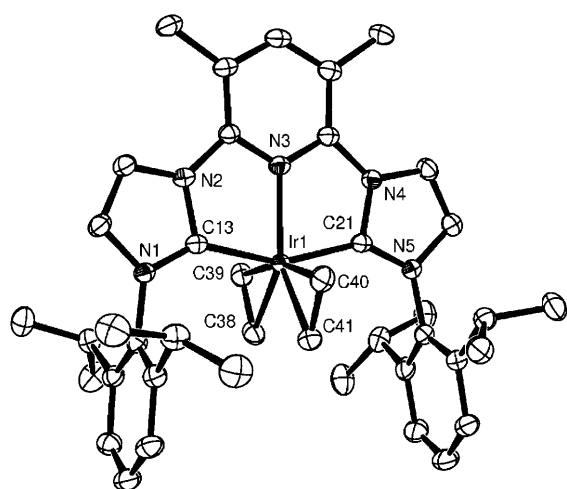


Figure 1. ORTEP representation of the cation in **4**. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Ir1–C13 2.019(3), Ir1–C21 2.018(3), C38–C39 1.439(5), C40–C41 1.422(4).

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

Substitution of the chloride ion in **2** by NaOiPr 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 KPF₆) to give **6** (Figures 3 and 4), a bimetallic PF₆[−] salt, containing one Ir^I center and one Ir^{III} center.

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 η³-allyl group, which originated from metalation of one *o*-

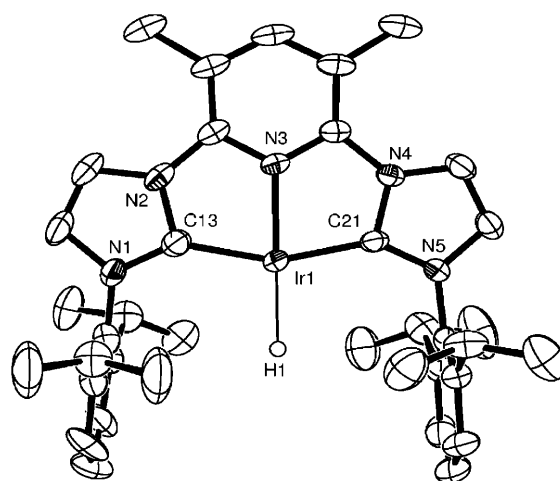


Figure 2. ORTEP representation of **5**. Thermal ellipsoids are set at 50% probability. Hydrogen atoms (with the exception of H1) are omitted for clarity. Selected bond lengths [Å]: C13–Ir1 1.972(4), C21–Ir1 1.964(4).

*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 η²-ethylene-like fashion, from the unsaturated backbone of the imidazol-2-ylidene, forming a bridge between the Ir^I and Ir^{III} centers.

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 η²-coordinated NHC [1.460(4) Å, as compared with 1.336(4) Å in C_{NHC}–N^{Me}–

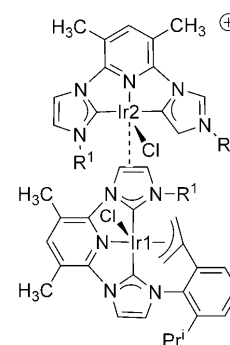


Figure 3. Diagram of **6**.

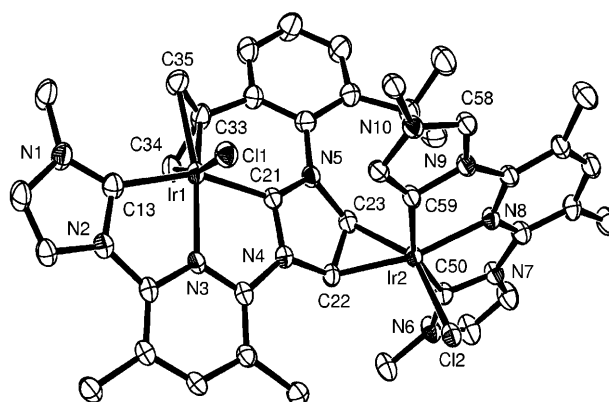


Figure 4. ORTEP representation of the cation in **6**. Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity. Only the *ipso* carbon of the aromatic substituents attached at N1, N6, and N10 is shown. Selected bond lengths [Å]: C13–Ir1 2.065(3), C21–Ir1 2.015(3), C50–Ir2 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 $[IrCl(coe)_2]$ (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 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, α = 105.8720(10), β = 101.4970(2), γ = 91.0240(10)°; V = 1998.5(2) Å³, 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, α = 83.460(2), β = 80.693(2), γ = 71.350(2)°; V = 1699.98(10) Å³, 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, α = 65.338(3), β = 70.541(3), γ = 66.844(3)°; V = 4364(2) Å³, 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 [$I > 2\sigma(I)$].

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