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Ligand Oxidation of a Deprotonated Bis(picolyl)amine Ir^{I}(cod) Complex

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Dedicated to Jan Reedijk on occasion of his retirement from the University of Leiden

The combination of transition-metal Lewis acidity and radical-type reactivity of "redox non-innocent" ligands bound to the same metal plays a pivotal role in the biochemistry of several important metalloenzymes, thus enabling them to perform transformations which would otherwise be difficult to perform. The catalytic mechanism of alcohol oxidation by galactose oxidase is probably the most well known.[1] Bio-inorganic chemists are successfully applying non-innocent or radical ligands to create catalytically active, and thus functional models of these enzymes.[1b] Therefore, it is to be expected that combining typical organometallic transformations with ligand-radical reactivity will lead to unexpected and new (catalytic) reactivity. In organometallic chemistry, however, the observation of ligand radicals is still rare. In this paper we show that the poly(picolyl)amine ligand can be transformed into a ligand radical, even in the coordination sphere of a coordinative unsaturated organometallic Ir^{I}(cod) fragment. The N-donor ligands poly(picolyl)amines and a variety of structurally closely related ligands are widely applied in coordination chemistry[2] and catalysis. Many first row transition-metal complexes (Fe, Cu, Mn) of these ligands are excellent structural and functional models for the active sites of a variety of enzymes, such as cytochrome C oxidase,[3] catalases,[4] Cu-based oxidases and oxygenases,[5] and non-heme Fe oxidases and oxygenases.[6] Also these ligands are valuable in late transition metal (organometallic) chemistry, especially in alkane oxidation (Ru),[7] olefin oxidation (Rh, Ir),[8] and stabilisation of reactive organometallic radical complexes (Rh, Ir).[9] Neutral poly(picolyl)amine ligands are generally quite robust "spectator" or "innocent" ligands, stable towards a variety of oxidizing and radical-like reagents. In fact, oxygenation of coordinated picolyl fragments in these and related ligands has been reported only in exceptional cases.[10] However, their stability or "chemical innocence" under basic conditions has not been explored in detail. Thus far, only limited examples of complexes containing deprotonated poly(picolyl)amine ligands have been reported. Obviously, amine deprotonation of these ligands is to be expected and easily leads to the formation of amido-bridged dinuclear species.[11] Amine-deprotonated bis(picolyl)amine (bpa) was recently used to stabilize a mononuclear gold(III) complex.[12] On the other hand, the "benzylic" methylene protons of this type of ligands are less acidic,[12] and we are thus not aware of any stable methylene deprotonated bis/tris-(picolyl)amine (bpa/tpa) complexes with the single exception of our recently reported compound $[Rh_2(\mu\text{-bpa}-2H)(nbd)_2]$.[13] In marked contrast, methylene deprotonated (picolyl)phosphane-type ligand (late) TM complexes have been reported,[14] and interestingly the resulting anionic ligands are not just "spectator" ligands; they directly participate in (catalytic) heterolytic H–H and C–H bond-breaking reactions.[15] Radical ligands are more reactive, and thus comparable cooperative substrate activation by the metal and a radical ligand should allow faster reactions and/or conversion of less reactive substrates. In general, radical ligands are fascinating because of their unusual redox properties, their ability to stabilize metals in unusual oxidation states,[16] and their ability to participate in (bio)catalytic reactions.[17]

In view of the importance of bpa-like ligands, we now report our findings on the deprotonation reactions of the

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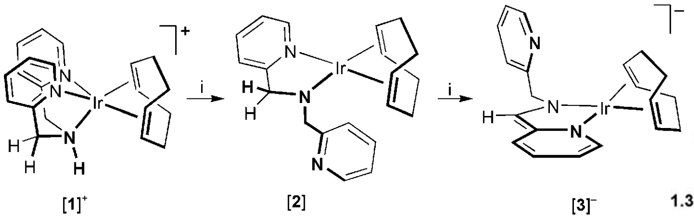
complex [Ir(bpa)(cod)]PF$_6$ that reveal the loss of innocence of the bis(picolyl)amine (bpa) ligand under basic aerobic conditions.

Treatment of [Ir(bpa)(cod)]PF$_6$ ([**1**]PF$_6$)[18] with two molar-equiv of potassium *tert*-butoxide (KO*t*Bu) in THF resulted in a color change from light-yellow to deep-red. NMR spectroscopical analysis indicated selective formation of the doubly deprotonated product [**3**]$^-$. Complex K[**3**] was isolated by recrystallization in THF/hexane as dark-red microcrystals. Besides the expected deprotonation of the weakly acidic amine proton, one of the methylene backbones of [**1**]$^+$ had also been deprotonated unexpectedly, resulting in formation of the anionic [Ir(bpa−2H)(cod)]$^-$ ([**3**]$^-$) (Scheme 1).



Scheme 1. Double deprotonation of [Ir(bpa)(cod)]$^+$, i) KO*t*Bu.

The reaction was found to occur stepwise through the mono-deprotonated intermediate amido compound [Ir(bpa−H)(cod)] (**2**), observable when using only one molar equivalent of KO*t*Bu. On a preparative scale, complex **2** can be straightforwardly prepared by reacting [{Ir(μ-OMe)(cod)}$_2$] with bpa (1:2 molar ratio) in diethyl ether, while K[**3**] was easily isolated from the reaction of **2** with one molar equivalent of KO*t*Bu, since only alcohols are produced in both reactions. Complex K[**3**] was found to be moisture-sensitive and easily protonated to complex **2** with acids.

Recrystallization of complex K[**3**] from THF/hexane rendered dark-red monocrystals; their X-ray structure[19] (see Figure 3) revealed polymer chain {K[**3**]}$_n$.

Complex {K[**3**]}$_n$ can be described as an electrostatically enforced host–guest complex in which the K$^+$ is embedded in the organometallic framework [Ir(bpa−2H)(cod)]$^-$. The organometallic host, [**3**]$^-$, (Figure 1) contains a square-planar iridium chelated by the double deprotonated {bpa−2H}$^{2-}$ ligand[20] and the diolefin 1,5-cyclooctadiene. Both the C5–C6 and the C6–N3 distances are unusually short, suggesting a considerable delocalization of electron density between these atoms. Within the pyridine ring, both C−N bonds and two C−C bonds become longer than the other two C−C bonds pointing to a substantial contribution of the resonance structures depicted in Figure 2.

The potassium cation is sandwiched by two five-membered metallacycles similar to a pentahapto cyclopentadienyl (η^5-Cp) ligand,[21] and shows an additional interaction with N2 (K−N2 2.782(9) Å). In addition, the metallacycle interacts, on both sides, with K$^+$ forming the "supersandwich" complex depicted in Figure 3. The angle at the potassium with the two centroids of the metallacyles is 139.6°, which is very different from the value of 180° expected for a typical sandwich compound. This is due to the distortion generated on the coordination sphere of K$^+$ by the additional interaction with N2. As a result, a regular zig–zag polymeric chain structure was formed (Figure 3). Overall, the structure of K[**3**] is related to the organic polymeric chain {K[(Me$_3$Si)C$_5$H$_4$]}$_n$.[22]

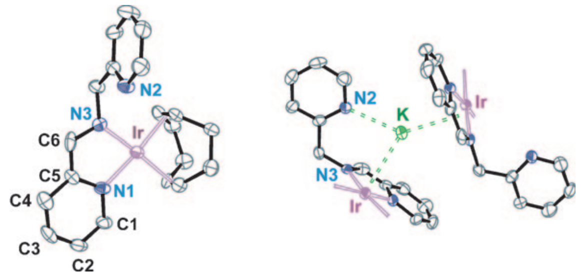


Figure 1. Structure (ORTEP at 50% level) of K[**3**] Left: geometry around Ir, right: geometry around K$^+$ (the cod ligands have been omitted for clarity). Selected lengths [Å] for K$^+$: K−N2 2.782(9), K−Ir 3.299(3) [3.362(3)], K−N1 3.150(9) [3.030(9)], K−C5 3.086(11) [3.027(11)], K−C6 3.024(11) [3.060(12)], K−N3 3.005(9)[3.103(8)] (distances to the unlabeled complex are in brackets).

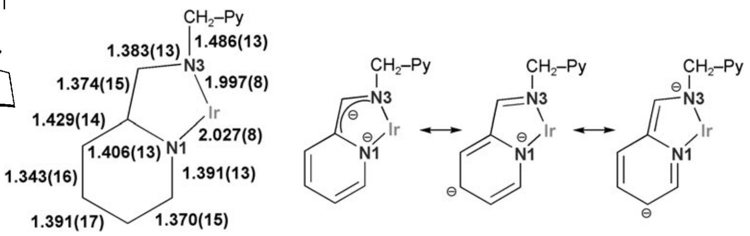


Figure 2. Left: selected distances for the {bpa−2H}$^{2-}$ ligand in [**3**]$^-$, right: main resonant forms of the {bpa−2H}$^{2-}$ ligand in the anion [**3**]$^-$.

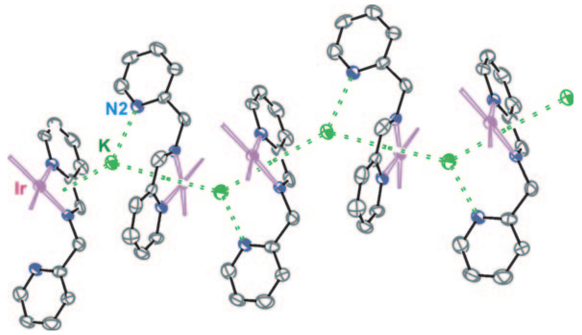


Figure 3. View of the coordination polymeric chain of the complex {K[**3**]}$_n$.

Aromatic five-membered rings sandwiching potassium ions are well-known in organic chemistry; around one hundred of this type of structures can be found in the CCDB. However, K$^+$–sandwich complexes involving metallacycles are hardly known and just two Zn complexes have been crystallographically characterized up to date.[23] Interestingly, these zincates contain 1,2-diamidoethene ligands (doubly reduced α-diimine ligands), which noticeably are redox active ligands. The binding mode of K^+ in K[**3**] may point to some aromatic character of the (bpa−2H)Ir chelate ring.[24] From the similarity of K[**3**] and the zincate ones, a "redox activity" of the $\{bpa-2H\}^{2-}$ ligand could be envisaged, and we indeed observe this behavior (see below).

The ^{1}H NMR spectrum of K[**3**] showed broad resonances at room temperature, which became sharp at −70 °C. At this temperature, the methine proton attached to C6 from the $\{bpa-2H\}^{2-}$ ligand was easily identified as a singlet at δ = 6.38 ppm. The signals of one of the two pyridine moieties of this new ligand are substantially upfield shifted, suggestive for increased electron density at the pyridyl moiety bound to the iridium. In particular, those corresponding to the protons attached to C3 and C2 were unusually upfield shifted ($\delta = 4.56$ and 3.91 ppm, respectively, see Supporting Information) in agreement with the resonance forms depicted in Figure 2. The dianionic charge of the $\{bpa-2H\}^{2-}$ ligand, introduced by the double deprotonation, is thus delocalized over the methine unit and the adjacent pyridyl group, and leads to a substantially increased donor capacity of the ligand. As a result, the electron-rich iridium center prefers to dissociate its other pyridyl fragment, which was coordinated in the starting material $[\mathbf{1}]^+$.

The easy double deprotonation of the bpa ligand bound to the electron-rich Ir center (with filled d_π orbitals repelling the increased π-electron density at the bpa−H and bpa−2H ligands) is remarkable and unexpected. It seems that increased Ir→C=C π-back donation to the cod double bonds upon deprotonation of the bpa fragment is at least in part responsible for the ease of these reactions. Deprotonation of $[\mathbf{1}]^+$ to **2** leads to dissociation of one of the pyridine arms, and thus the average Ir→C=C π-back donation hardly changes (average olefinic ^{13}C chemical shifts: $[\mathbf{1}]^+$: δ = 56.6 ppm; **2**: δ = 59.0 ppm). However, the two cod olefins in **2** are non-equivalent, and not exchanging on the NMR timescale, with substantially lower field ^{13}C chemical shifts for the olefinic carbons *trans* to the anionic amido fragment (δ = 53.5 ppm) compared with the olefinic carbons *trans* to the neutral Py fragment (δ = 64.4 ppm). After the second deprotonation in formation of $[\mathbf{3}]^-$, the two olefinic fragments are shifted further upfield, but now have almost identical chemical shifts (δ = 48.0 and 46.0 ppm). These data suggest that the increased π-electron density at Ir (introduced by unfavourable mixing of the Ir d_π orbitals with the increased ligand π density upon deprotonation) is effectively passed-through from Ir to the olefinic double bonds of cod, thus explaining the relatively easy (double) deprotonation of $[(bpa)Ir^I(cod)]^+$.

The envisaged ligand oxidation of K[**3**] was revealed from the redox behavior towards oxidizing reagents. Thus, in situ chemical oxidation of K[**3**] with one equivalent of Ag^+, followed by rapid-freeze quenching, allowed us to detect the neutral 1e$^-$ oxidized complex [Ir(bpa−2H)(cod)] $[\mathbf{4}]^\bullet$ by EPR spectroscopy. The EPR spectrum in frozen solution revealed a slightly rhombic signal, with g values very close to g_e, suggesting that the unpaired electron of $[\mathbf{4}]^\bullet$ is mainly located at the $\{bpa-2H\}^{\bullet-}$ ligand (Figure 4).

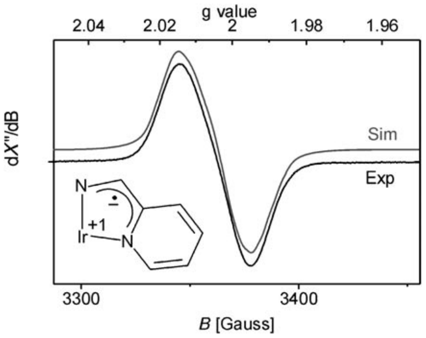


Figure 4. EPR spectrum of $[\mathbf{4}]^\bullet$. Conditions: freq. = 9.43194 GHz, T = 20 K, att. = 30 dB, mod. amp. = 3 G. The simulated spectrum was obtained with the following g-tensor: $g_{11} = 2.015$, $g_{22} = 2.004$, $g_{33} = 1.994$.

This assignment is in good agreement with the calculated (DFT) spin density distributions of $[\mathbf{4}]^\bullet$ (Figure 5). The unpaired electron is delocalized over the imine and pyridine fragments, but mainly resides at the "α-diimine" fragment. Part of the spin density is also located at the C2 and C3 atoms (Figure 5). There is virtually no spin density at the metal and thus, $[\mathbf{4}]^\bullet$ is best described as a ligand radical complex. Rare examples of related first-row TM ligand radical complexes, obtained by chemical reduction of pyridine-2-imine complexes, were recently disclosed by Wieghardt et al.[16]

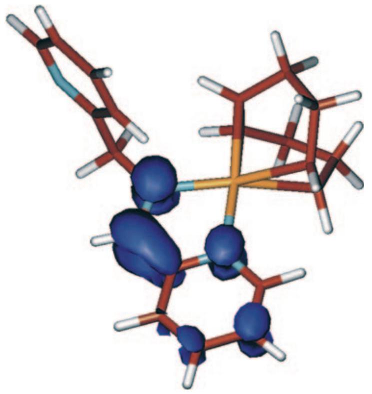


Figure 5. Spin density plot of $[\mathbf{4}]^\bullet$.

Complex $\mathbf{4}^\bullet$ is relatively stable in dilute solutions at room temperature, but slowly (within hours) decomposes at higher concentrations, presumably via a bimolecular pathway to yield (a) yet unidentified product(s). The fate of $\mathbf{4}^\bullet$ is currently under investigation.

A THF solution of diamagnetic K[**3**] exposed to air, for a short period, produced an identical EPR spectrum as shown in Figure 4, first growing in intensity then decreasing again in time upon prolonged exposure to air. This is quite remarkable, because in our experience four- and five-coordinate $\mathrm{Rh^I}$(cod) and $\mathrm{Ir^I}$(cod) complexes with N-donor ligands tend to easily react with O_2 to form 2-metallaoxetanes and related species.[8] Considering the presence of the coordinatively unsaturated and electron rich, oxidizable $\mathrm{Ir^I}$(cod) fragment, it is thus quite remarkable that reaction of $[\mathbf{3}]^-$ with O_2 leads to formation of a ligand radical derived from bpa instead of the expected oxygenation of the $\mathrm{Ir^I}$(cod) fragment. We are currently investigating the reactivity of K[**3**] towards O_2 in more detail.

In conclusion, we demonstrated that $\mathrm{Ir^I}$(cod) complexes with bpa ligands are easily doubly deprotonated. The first and expected deprotonation occurs at the amine donor, followed by a second deprotonation at a neighboring methylene unit. Subsequent chemical oxidation by Ag^+ or O_2 leads to a ligand radical complex. This sequence clearly demonstrates the chemical reactivity of bpa and the redox activity of the deprotonated bpa ligand. This unusual behaviour has important chemical consequences: Although poly(picolyl)amine ligands are widely used as stable, robust and non-reactive ligands, they may not always be as "innocent" as they seem.

Experimental Section

[Ir(bpa−H)(cod)] (2): A suspension of [{Ir(μ-OMe)(cod)}] (200.0 mg, 0.30 mmol) in diethyl ether (20 mL) was slowly added to a solution of bis(picolyl)amine (bpa) (112 μL, 0.60 mmol) in diethyl ether (4 mL). An immediate red solution was formed after mixing the reagents. The solution was evaporated to ca. 5 mL and kept undisturbed at −20 °C overnight to render dark-red crystals, which were washed with cold hexane (3×3 mL) and vacuum-dried. Yield: 233.4 mg (78 %). ^{1}H NMR (500 MHz, [D_8]toluene, −40 °C): $\delta = 8.35$ (d, $J = 3.9$ Hz, 1 H, H^{A1}), 7.58 (d, $J = 7.8$ Hz, 1 H, H^{A4}), 7.34 (d, $J = 5.6$ Hz, 1 H, H^{B1}), 6.85 (td, $J = 7.6$, 1.7 Hz, 1 H, H^{A3}), 6.37 (t, $J = 6.1$ Hz, 1 H, H^{A2}), 6.32 (t, $J = 7.3$ Hz, 1 H, H^{B3}), 6.10 (d, $J = 7.8$ Hz, 1 H, H^{B4}), 5.82 (d, $J = 6.3$ Hz, 1 H, H^{B2}), 4.56, 3.91 (2 s, 2×1 H, CH_2 bpa), 3.63, 2.67 (2 m, ×2 H, HC=cod), 2.32, 2.17 (2 m, ×2 H, CH_2^{exo} cod), 1.73, 1.63 ppm (2 m, ×2 H, CH_2^{endo} cod); ^{13}C{^{1}H} NMR (500 MHz, [D_8]toluene, −40 °C): $\delta = 171.1$ C^{A5}, 164.6 C^{B5}, 149.2 C^{A1}, 145.1 C^{B1}, 136.0 C^{A3}, 135.0 C^{B3}, 121.3 C^{B2}, 121.1 C^{A2}, 120.3 C^{A4}, 119.8 C^{B4}, 69.2 and 59.8 CH_2 bpa, 64.4 and 53.5 HC=cod, 32.6 and 32.1 ppm CH_2 cod (see Figure 6 for the labeling of protons and carbons); elemental analysis calcd (%) for $C_{20}H_{24}N_3Ir$ (498.6): C 48.17, H 4.85, N 8.43; found: C 48.25, H 4.73, N 8.36.

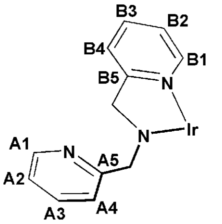


Figure 6. Labeling of protons and carbons in complexes **2** and K[**3**].

K[Ir(bpa−2H)(cod)] (K[3]): A brown solution of [Ir(bpa−H)(cod)] (**2**) (75.0 mg, 0.15 mmol) in THF (4 mL) was treated with solid KO*t*Bu (20.2 mg, 0.18 mmol). After stirring for 2 h at RT, the resulting red-brown solution was carefully layered with hexane (10 mL) and kept undisturbed at −20 °C for 3 d. The brown-red crystals were separated by decantation, washed with cold diethyl ether (3 mL), then with hexane (2×3 mL) and vacuum-dried. Yield: 40.2 mg (49.5 %). ^{1}H NMR (400 MHz, [D_8]THF, −70 °C): $\delta = 8.36$ (d, $J = 4.0$ Hz, 1 H, H^{A1}), 7.61 (td, $J = 7.3$, 1.5 Hz, 1 H, H^{A3}), 7.09 (m, $H^{A2\,A4}$), 6.72 (d, $J = 6.2$ Hz, 1 H, H^{B1}), 6.39 (d, $J = 8.8$ Hz, 1 H, H^{B4}), 6.11 (s, 1 H, N=CH), 5.50 (t, $J = 7.3$ Hz, 1 H, H^{B3}), 4.71 (t, $J = 6.2$ Hz, 1 H, H^{B2}), 4.64 (s, 2 H, CH_2 bpa), 3.00, 2.56 (2 m, ×2 H, HC=cod), 2.07, 1.96 (2 m, ×2 H, CH_2^{exo} cod), 1.71 ppm (m, 4 H, CH_2^{endo} cod; ^{13}C{^{1}H} NMR (400 MHz, [D_8]THF, −70 °C): $\delta = 163.6$ C^{A5}, 146.2 C^{A1}, 140.1 C^{B1}, 134.4 C^{A3}, 134.4 C^{B5}, 119.6 C^{A4}, 118.9 C^{A2}, 118.1 C^{B4}, 117.2 N=CH, 113.1 C^{B3}, 94.9 C^{B2}, 56.7 CH_2 bpa, 48.8 and 46.0 HC=cod, 30.9 and 30.7 ppm CH_2 cod (see Figure 6 and Supporting Information for the labeling of protons and carbons); elemental analysis calcd (%) for $C_{20}H_{23}N_3IrK$ (536.7): C 44.76, H 4.32, N 7.83; found: C 44.69, H 4.22, N 7.77.

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[19] CCDC 646547 (K[**3**]}$_n$) contains 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

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[21] The distances between the centroid of the metallacylces (Ct) and K^+ are 2.794 and 2.788 Å, with a ring-slippage of 0.132 and 0.161 Å, respectively. The angles formed by the K–Ct line with the best plane of the metallacycles were found to be 87.2 and 86.7°, respectively.

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