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Bridging Amido Complexes of Dirhodium and Diiridium Tetracarbonyls

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We wish to report the synthesis and structural characterization of the first examples of amido-($^-$NHR-) bridged dinuclear rhodium(I) and iridium(I) complexes supported only by carbonyl ligands. The vast majority of amido complexes are known for the early transition metals,[1] where the metal-nitrogen bond is usually stabilized by strong π donation from the amido nitrogen. Interest in the preparation of late transition metal-amide complexes has grown steadily in recent years, with emphasis on the study of the metal-nitrogen bond reactivity in these complexes.[2] We hope that, similar to the chloro-bridged rhodium and iridium carbonyl complexes, the complexes reported here will allow access to a large number of new mononuclear and dinuclear amido complexes which will provide further insight into the chemistry of the late transition metal-nitrogen bond.

The reaction between NaOR (R = Me, Et or Ph) and *cis*-$MCl(CO)_2(NH_2R')$[3] (R' = Ph, *p*-tolyl when M = Rh, and R' = *p*-tolyl when M = Ir) in toluene or THF produces $M_2(CO)_4(\mu\text{-}NHR')_2$ in high yields. The reaction, depicted in (1), can proceed

$$cis\text{-}M(CO)_2Cl(H_2NR') + NaOR \rightarrow {}^1/_2M_2(CO)_4(\mu\text{-}NHR')_2 + NaCl + ROH \quad (1)$$

R = Me, Et, or Ph; M = Ir, R' = *p*-tolyl (**1**);
M = Rh, R' = *p*-tolyl (**2a**); M = Rh, R' = Ph (**2b**)

through either Cl^- for ^-OR substitution, followed by deprotonation of the amine by ^-OR, or direct dehydrohalogenation by NaOR. Experiments are underway to differentiate between the two possibilities. All of the complexes have been characterized by elemental analysis, NMR, and IR, and the solid-state structure of **1** has been determined by X-ray diffraction studies. The Rh complexes can also be prepared by reacting LiNHR' with $Rh_2(\mu\text{-}Cl)_2(CO)_4$. It is interesting to point out that a similar reaction between LiNHR' and $Rh_2(CO)_2Cl_2(dppm)_2$ (dppm = (diphenylphosphino)methane) results in the formation of a μ-imido complex $Rh_2(\mu\text{-}NR')(CO)_2(\mu\text{-}dppm)_2$ or its tautomer $Rh_2(\mu\text{-}NHR')(CO)_2(\mu\text{-}dppm)(\mu\text{-}dppm')$, where dppm' is the deprotonated bis(phosphine), or mixtures of the two.[2d] We do not see any indication of the formation of imido complexes in our reactions.

The solution IR spectra of the amido complexes in the carbonyl region show three bands,[4] which is typical of $M_2(\mu\text{-}X)_2(CO)_4$ type complexes. Curiously, ν(N-H) bands were not observed in the expected region of the IR spectrum. The ^1H NMR spectra of the complexes are quite straightforward.[5] The strongest evidence for the presence of an amido group in these complexes comes from the appearance of the -NH- resonance at 3.40 ppm for **1**, 2.48 ppm for **2a**, and 2.50 ppm for **2b**. All of these resonances are fairly broad, and each integrate to one proton. The $-NH_2$ resonances in the parent complexes, *cis*-$M(CO)_2Cl(H_2NR)$, are all downfield compared to the above -NH- resonances.

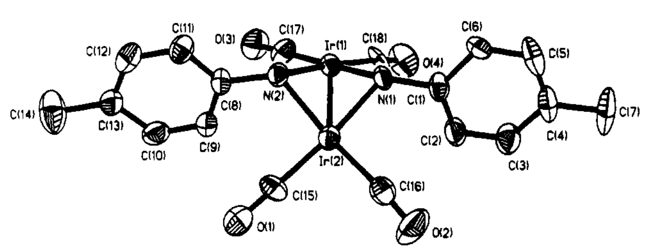

Figure 1. ORTEP plot of **1**(T) showing 50% probability of the thermal ellipsoids. Selected bond distances (Å) and angles (deg) for **1**(T) (values for **1**(O) are given in parentheses): Ir(1)-Ir(2) = 2.933 (1) (2.968 (2)), Ir(1)-N(1) = 2.11 (1) (2.09 (2)), Ir(1)-N(2) = 2.11 (2) (2.13 (3)), Ir(2)-N(1) = 2.07 (2) (2.16 (2)), Ir(2)-N(2) = 2.09 (2) (2.08 (2)), N(1)-C(1) = 1.43 (2) (1.42 (5)), N(2)-C(8) = 1.45 (2) (1.46 (4)), Ir-C(av) = 1.86 (1.86); Ir(1)-N(1)-Ir(2) = 89.0 (4) (88.4 (10)), Ir(1)-N(2)-Ir(2) = 88.6 (7) (89.6 (10)), N(1)-Ir(1)-N(2) = 75.1 (6) (75.6 (10)), N(1)-Ir(2)-N(2) = 76.4 (6) (75.1 (10)), Ir(1)-N(1)-C(1) = 120.3 (13) (116.7 (18)), Ir(2)-N(1)-C(1) = 123.9 (14) (117.5 (18)), Ir(1)-N(2)-C(8) = 118.7 (13) (118.3 (17)), Ir(2)-N(2)-C(8) = 123.7 (14) (119.9 (18)), N(1)-Ir(1)-C(17) = 172.9 (11) (175.2 (13)), N(1)-Ir(2)-C(15) = 172.9 (7) (171.8 (14)), N(2)-Ir(1)-C(18) = 174.2 (6) (174.6 (15)), N(2)-Ir(2)-C(16) = 174.1 (8) (174.8 (13)), C(17)-Ir(1)-C(18) = 87.1 (11) (85.6 (19)), C(15)-Ir(2)-C(16) = 88.6 (10) (88.0 (16)).

All three complexes can be obtained in crystalline form from mixtures of toluene and hexane. Complexes **2a** and **2b** form orange-red microcrystals and were not suitable for X-ray diffraction studies. Complex **1** crystallizes as two polymorphs, yellow (triclinic), **1**(T), and purple (orthorhombic), **1**(O), which were characterized by single-crystal X-ray diffraction studies.[6] There are no significant differences in the molecular geometry in the two crystal forms. However, the molecules pack in strikingly different fashions in the two crystals, and will be discussed later. An ORTEP plot of **1**(T) is shown in Figure 1. The molecule contains roughly two mirror planes, one along the Ir-Ir vector and the other perpendicular to it and containing the two bridging nitrogen atoms and the phenyl rings. The angles around each

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(3) (a) For the synthesis of *cis*-$Ir(CO)_2Cl(NH_2R)$, see: Klabunde, U. *Inorg. Synth.* **1974**, *15*, 82. (b) For the synthesis of *cis*-$Rh(CO)_2Cl(NH_2R)$, see: Vallarino, L. M.; Sheargold, S. W. *Inorg. Chim. Acta* **1979**, *36*, 243.

(4) **1** in CH_2Cl_2: 2072 (m), 2051 (vs), 1991 (vs) cm^{-1}. **2a** in CH_2Cl_2: 2077 (m), 2060 (vs), 2004 (vs) cm^{-1}. **2b** in CH_2Cl_2: 2079 (m), 2061 (vs), 2005 (vs) cm^{-1}.

(5) All ^1H NMR spectra were taken in $CDCl_3$ and chemical shifts are reported vs TMS at δ 0. **1**: 7.05 (s, 4 H, C_6H_4Me), 3.40 (br s, 1 H, *H*N-), 2.33 (s, 3 H, C_6H_4Me). **2a**: 7.10, 6.93 (AB quartet, 4 H, C_6H_4Me), 2.48 (br s, 1 H, *H*N-), 2.25 (s, 3 H, C_6H_4Me). **2b**: 7.16, 6.90 (m, 5 H, C_6H_5), 2.50 (br s, 1 H, *H*N-).

(6) Crystal data for **1**(T): $C_{18}H_{14}Ir_2N_2O_4$, triclinic, $P\bar{1}$, a = 9.718 (3) Å, b = 10.414 (3) Å, c = 11.897 (3) Å, α = 105.82 (2)°, β = 100.65 (2)°, γ = 115.19 (2)°, V = 983.6 (6) Å^3, Z = 2, D_x = 2.386 g cm^{-3}, $R(F)$ = 6.95%, $R_w(F)$ = 8.18% for 3401 independent, observed data (Siemens P4, 2θ(max) = 60°, Mo Kα, 294 K). Crystal data for **1**(O): $C_{18}H_{14}Ir_2N_2O_4$, orthorhombic, *Pccn*, a = 9.361 (2) Å, b = 16.372 (3) Å, c = 25.615 (6) Å, V = 3925.4 (15) Å^3, Z = 8, D_x = 2.392 g cm^{-3}, $R(F)$ = 6.44, $R_w(F)$ = 7.81% for 1320 independent, observed data (Siemens P4, 2θ(max) = 45°, Mo Kα, 295 K). For both structures empirical methods were used to correct for absorption. All non-hydrogen atoms of **1**(T) were refined anisotropically, while, to conserve data, only the Ir and O atoms of **1**(O) were refined anisotropically.

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iridium atom deviate significantly from an ideal value. The largest deviations are observed for the N(1)–Ir(1)–N(2) (75.1 (6)° in **1**(T) and 75.6 (10)° in **1**(O)) and N(1)–Ir(2)–N(2) (76.4 (6)° in **1**(T) and 75.1 (10)° in **1**(O)) angles. The trigonal-pyramidal coordination (ignoring the hydrogen) around each nitrogen atom has also flattened considerably. These deviations seem to result from steric interaction between the phenyl rings and the carbonyl ligands, as suggested by space-filling models of the molecule. Similar angle distortions have been observed in the complex $Ir_2(CO)_2(\mu\text{-}S^tBu)_2[P(OMe)_3]_2$.[7] As expected, each iridium atom sits in a roughly square-planar arrangement. The two square planes are not coplanar, interesecting at an angle of 124.6°, thus making it possible for the two iridum atoms to come within the metal–metal single-bond distance. The metal–metal separation in **1**(T) is 2.933 (1) Å, whereas that in **1**(O) is slightly longer, 2.968 (2) Å. These intermetallic contact distances are on the shorter side of the distances observed for dinuclear Rh(I) and Ir(I) complexes of the type $M_2(\mu\text{-}X)_2L_4$. Some representative values are as follows: $Rh_2(\mu\text{-}Cl)_2(CO)_4$, 3.12 Å;[8] $Rh_2(\mu\text{-}Cl)_2[P(O^iPr)_3]_4$, 3.431 Å;[9] $Ir_2(\mu\text{-}S^tBu)_2(CO)_2[P(OMe)_3]_2$, 3.216 Å[7] and $Rh_2(\mu\text{-}H)(\mu\text{-}NMe(4\text{-}C_6H_4Cl))[P(O^iPr)_3]_4$, 2.844 Å.[9]

The packings of the molecules of **1** in the two polymorphs are significantly different and are shown in Figure 1S of the supplementary material. In the yellow form, **1**(T), the molecules pack forming pairs with close intermolecular Ir···Ir contact of 3.98 Å. In the purple form, **1**(O), the molecules aggregate in an infinite chain with intermolecular metal–metal contact of 3.75 Å between adjacent molecules in the whole chain. Such stacking of square-planar environments has previously been observed in a number of rhodium and iridium complexes and is thought to produce the unusual variety of color and electronic conduction in many of these complexes.[10]

The visible spectra of **1**(T) and **1**(O) are different in the solid state, as expected, but identical in solution. The major difference in the spectra (Figure 2S of the supplementary material) is the intensity of the low-energy absorption band at 552 nm, being strongest for the purple solid.[11] The intensity of this band in the spectrum of the yellow solid is somewhat analogous to that found in the solid-state spectra of **2a** and **2b**. Solutions of **1**(T) and **1**(O), as well as those of **2a** and **2b**, in CH_2Cl_2 show no absorption band at wavelengths higher than 400 nm. These results clearly suggest that the long-range intermolecular contact observed for **1** in the solid state must give rise to the low-energy transition and that the intermolecular contacts disappear in solution, as evidenced by the disappearance of the low-energy band in solution. The fact that the 552-nm band for the purple crystal has the same energy, only different intensity, as compared to that for the yellow crystal only implies that long-range electron delocalization does not exist in the purple solid, as might have been expected on the basis of its extended array of metal–metal contacts. A shift of the band to lower energy would have occurred for any significant electron delocalization over the whole array.

The complexes are remarkably air stable, both in solution and in the solid state. Several reactions are underway. In particular, we are investigating means to split the dimer to give monomeric amido complexes. We are also attempting deprotonation of the μ-NHR group to obtain imido moieties. Oxidative addition reactions with H_2, X_2 (X = Cl, Br, and I), and MeI are also being investigated. We obtain clean reactions of **1** with halogens, and spectral data suggest the formation of $Ir_2X_2(CO)_4(\mu\text{-}NH(p\text{-}tolyl))_2$ and $Ir_2X_4(CO)_4(\mu\text{-}NH(p\text{-}tolyl))_2$. Deprotonation of the μ-amido group in these halogenated complexes is currently being investigated.

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Supplementary Material Available: Molecular packing diagrams of **1**(T) and **1**(O) (Figure 1S), visible spectra of **1** (Figure 2S), and tables giving details of the X-ray data collection and refinement, atomic coordinates, anisotropic thermal parameters, bond distances and angles, and hydrogen atom parameters for both **1**(T) and **1**(O) (13 pages). Ordering information is given on any current masthead page.

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(11) Solid-state visible spectra were obtained from pellets in KBr which were of equal thickness and concentration.