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A unique six-membered chelated iridium complex†

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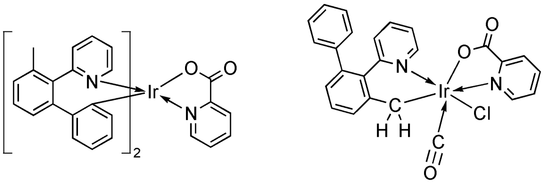
The reaction of 2-(3-methylbiphenyl-2-yl)pyridine with $IrCl_3 \cdot nH_2O$ in the presence of water incorporates a tightly bonded CO at the iridium center; in the subsequent reaction with picolinic acid a complex revealing an unusual CH activation of a methyl group is formed.

Late transition-metals such as Rh, Pt and Ir exhibit interesting properties. Among those properties, catalytic activity such as selective CH activation is most attractive to the synthetic chemist. Up to today there has been no general solution available for a catalytic functionalization process of unactivated sp^3 CH bonds.[1] In addition, various complexes of these metals can also be employed in OLEDs (organic light-emitting diodes) as high efficient triplet emitting materials.[2] Due to their significant spin–orbit coupling second and third row transition metals are most effective in harvesting the efficiency limiting triplet states.

We were searching for new materials that are applicable in OLEDs and were stimulated by a patent containing an interesting structural motif of a tweezer-like metal complex (an example is shown in Fig. 1).[3] The depicted idea of the ligand embracing the metal center for use as an emitter in OLEDs was related to some of our work.[4]



1 **2**

Fig. 1 Structures of a proposed tweezer-like metal complex **1** from a patent[3] and of isolated complex **2**.

We focused on complex **1** from the literature[3] and since no reaction details were given, we conducted the synthesis according to the following procedures. The ligand 2-(3-methylbiphenyl-2-yl)pyridine **3** was prepared according to literature methods[5] and obtained in an overall yield of 23% after HPLC purification. The cyclometalation was planned with regard to the expected products **4** and **1** as a two step reaction (Scheme 1). The first step was carried out following procedures from Nonoyama[6] leading to a μ-chloro-bridged dimer whereas the second step followed mild room temperature procedures from Coppo *et al.*[7] preventing scrambling of the ligands.

We characterized our isolated product **2** from the second step (14% yield) and found a strong band at 2021 cm^{-1} in the IR spectrum, indicating a CO moiety in the molecule. The NMR spectra displayed a large number of signals indicating an unsymmetric molecule.‡ Based on our experience with heteroleptic complexes, such as the proposed complex **1**, we expected two independent sets of signals originating from the ligand **3**. Instead we found only one set of signals and also the methyl group disappeared. We concluded that the obtained product was not consistent with the proposed structure **1**, and subjected it to X-ray analysis, revealing an unexpected and unique structure **2** (Fig. 2) consisting of a six-membered chelated iridium complex.§ The results were finally confirmed by repetition of the reactions.

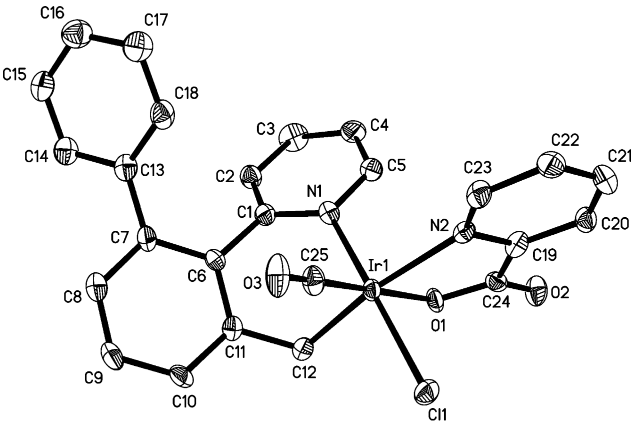


Fig. 2 ORTEP representation of the complex **2** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Ir1–C25 = 1.835(7), C25–O3 = 1.134(8), Ir1–Cl1 = 2.3392(15), Ir1–C12 = 2.070(6); N1–C1–C6–C11 = −45.7(8); O1–Ir1–N2 = 78.33(18).

In order to understand the reaction we returned to the precursor **4** or **5** from the first step. We were not able to crystallize the compound, but IR investigations showed evidence that the CO is already inserted in this step. A fairly strong band, weaker than the CO band of **2**, was observable at 2025 cm^{-1}, suggesting that the CO bonding modes are closely related to each other (see also ref. 8 for a review on vibrational frequencies in binary unsaturated transition-metal carbonyls).

Given that our reactions were carried out in a N_2 atmosphere, insertion of gaseous CO as often described in the literature[9] is

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† Electronic supplementary information (ESI) available: Experimental procedures for preparation of compounds **2**, **3** and **5a**, detailed spectroscopic data. CCDC reference number 675630. For ESI or crystallographic data in CIF or other electronic format see DOI: 10.1039/b807735p

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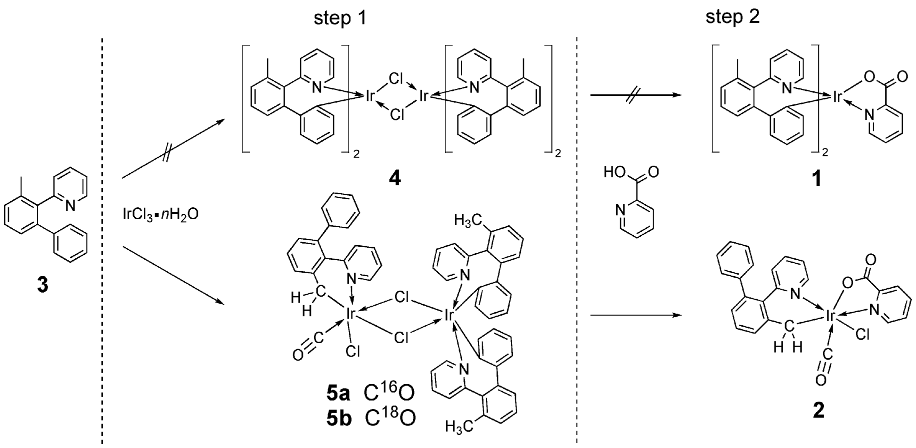

Scheme 1 Expected (upper path) and observed (lower path) reaction together with proposed intermediate products **4**, **5a** and **5b**. Compound **2** was only synthesized from intermediate product **5a**.

excluded. Initially we focused on the starting material $IrCl_3·nH_2O$. We examined the employed portion by IR spectroscopy and found only a weak signal at 2100 cm^{-1}, eliminating this material as the source of CO. Since CO was inserted in the first step, we focused on water as the source of oxygen in the CO. Several groups have monitored and investigated the incorporation of CO into iridium complexes with the aid of ^{18}O-labeled water, demonstrating that the oxygen originates from water.[10] We thus performed the first reaction step by replacing $H_2{}^{16}O$ (leading to compound **5a**) with $H_2{}^{18}O$ (leading to compound **5b**) and subsequently identified a shift of the CO band from 2025 to 1985 cm^{-1} for the first step (IR results are shown in Fig. 3). This result is in accordance with the theoretically calculated shift to 1977 cm^{-1}.[8]

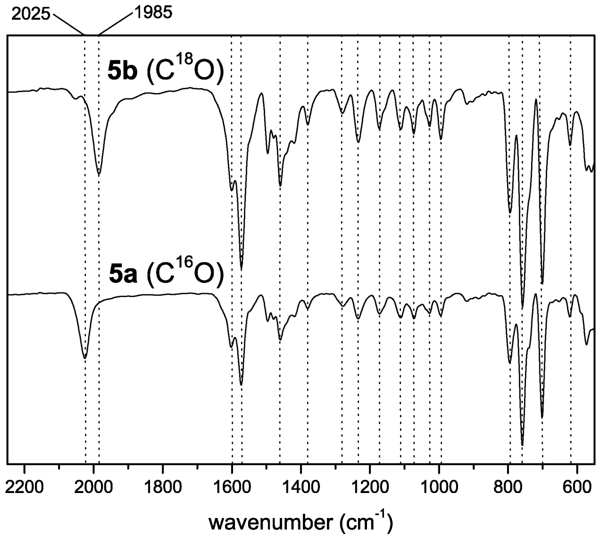

Fig. 3 IR spectra of compounds **5a** and **5b** demonstrating shift of the CO band around 2000 cm^{-1} for reaction with $H_2{}^{18}O$ (upper graph) and $H_2{}^{16}O$ (lower graph).

According to ref. 10 the source of carbon is an alkyne which is apparently not present in our case. We therefore considered two options for the source of the carbon: the solvent 2-ethoxyethanol and the methyl group of the ligand **3** itself. Comparable to the experiments with $H_2{}^{18}O$ a direct proof would ask for ^{13}C-labeled ligand **3** and ^{13}C-labeled solvent. Since both compounds are impractical we decided to perform a series of experiments to indirectly narrow down the source of the carbon. At first we examined the aqueous filtrate from step 1 to see if we could find evidence for a demethylation of **3**. According to GC-MS analysis only **3**, which has been used in excess, can be found. Then we changed the solvent to phenol, di-*n*-butyl ether and diethylene glycol dimethyl ether (diglyme) to examine the influence thereof. Generally the yield of precipitable products decreased in all cases. We compared the ^1H NMR spectra (especially the methylene protons) and the IR spectra (especially the CO band) of all reactions performed and found, that with the exception of 2-ethoxyethanol none of the other solvents led to the occurrence of a methylene bridge and a CO moiety. In addition the fingerprint region indicates a closely related cyclometalation of all reactions (a comparison of ligand **3** and two performed reactions is shown in Fig. 4). In another reaction we changed the ratio of **3** and

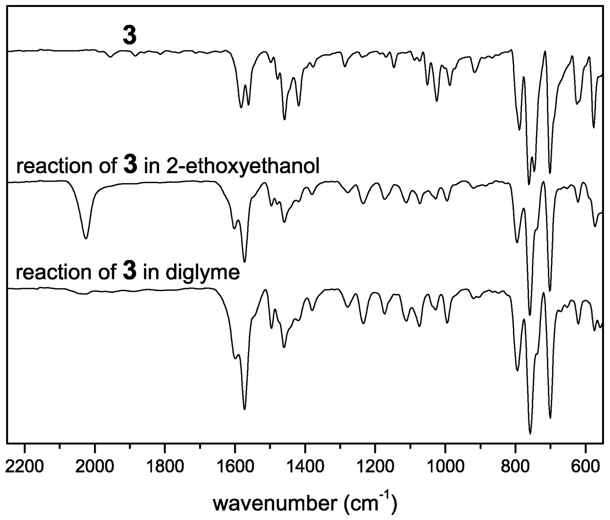

Fig. 4 IR spectra of compound **3** and products of reaction of **3** in 2-ethoxyethanol and in diethylene glycol dimethyl ether (diglyme) as solvents. The middle and lower graph show a similar change of the fingerprint region compared to starting material **3** implying a closely related cyclometalation. The lower graph exhibits an unambiguous lack of a CO band at 2025 cm^{-1} compared to the middle graph.

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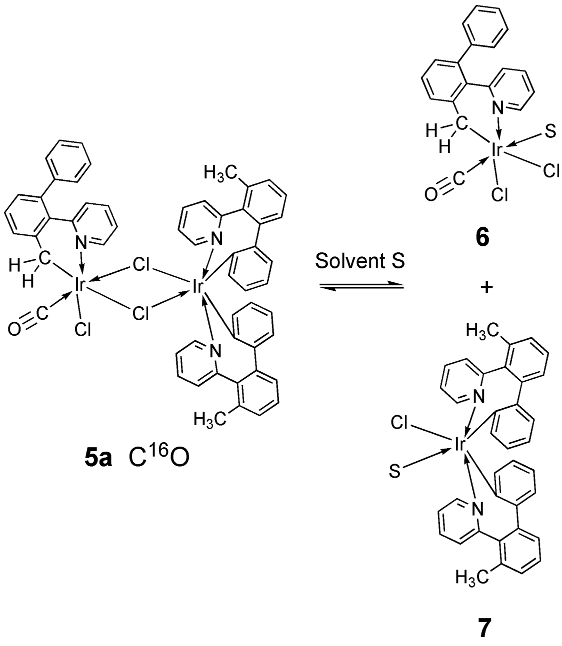
$IrCl_3 \cdot nH_2O$ from 2 : 1 to 1 : 1. We found a decrease in the yield of more than 50% and no evidence for a decrease of the CO content in **5a**. To rule out hard to detect impurities in the solvent as the source of carbon we also performed a reaction with a portion of the solvent from a different manufacturer. The reaction led to comparable results to those received with the solvent from the initial manufacturer. These results indirectly prove, that the solvent 2-ethoxyethanol is the source of carbon and in addition we learn, that the formation of CO and the activation of the methyl group are closely related to each other.

Furthermore we examined and compared our NMR and IR results of compounds **2**, **3** and **5a**. The NMR spectra of **5a** revealed two types of ligand or types of bonding to the metal center with a ratio of 1 : 2, whereas only one ligand is cyclometalated *via* a methylene bridge (shown by the characteristic and isolated signals of the magnetically inequivalent methylene protons around 4.3 and 3.9 ppm). We therefore propose the intermediate products **5a** and **5b** to be unsymmetric (Scheme 1). A splitting of **5a** as described by Gill *et al.*[11] and used by Mirabelli and Sneddon[12] would lead to solvent-stabilized intermediates **6** and **7** (Scheme 2). Since only **6** can react to produce **2** we find an explanation for the low yield of the reaction. What happens to the other half of the μ-chloro-bridged dimer **5a** remains unclear. Due to the tensed situation of these tweezer-like ligands in a complex a purely dative bonding mode of the pyridine nitrogen atom towards the center is conceivable. This weak interaction would in the end lead to an insoluble iridium salt and unreacted ligand **3**. This speculation is certainly based on the CH activation as the rate limiting step.



Scheme 2 Solvent-induced splitting of the μ-chloro-bridged dimer **5a** explaining the low yield.

Complex **2** exhibits some interesting structural motifs. The most striking feature is the six-membered ring containing the iridium and a methylene group. The necessary CH activation as well as the synthesis and incorporation of CO are attributable to the catalytic activity of iridium. The cyclometalating ligand **3** can be reduced to a bidentate *o*-tolyl-pyridine ligand that coordinates *via* the nitrogen of the pyridine ring and the alkyl group of the toluene ring. To the best of our knowledge only two complexes, one with a manganese center and another with a palladium center, share this rare motif with the present complex **2**.[13] Even six-membered rings without participation of alkyl groups are scarce. Only one series of complexes with a six-membered ring containing an iridium center is known to us.[14] The above mentioned manganese complex described by Djukic *et al.*[13a] was an unexpected formation obtained in 5% yield, whereas Stoccoro *et al.*[13b] intended to synthesize a complex coordinating *via* a methylene group. In order to optimize the creation of such bonds they used a palladium based precursor with a methyl group as one of the ligands and added a designed bidentate ligand with a free tolyl or a xylyl group to obtain a fixed system. Presumably a hydrogen from the methyl group of the tolyl or xylyl group is then transferred to the methyl ligand, whereas methane will be released and the bond formed.

The other feature is the Ir(CO)Cl moiety which can often be found in various metal complexes. CO can on the one hand stabilize a metal complex and on the other hand easily be replaced by other ligands or leave a vacant position for catalytic processes. In addition CO can be used as a structural probe. The group of Yersin[15] recently compared the commonly used OLED emitting material $Ir(ppy)_3$ with $Ir(ppy)_2(CO)Cl$, where one of the three bidentate phenylpyridine rings (ppy) is replaced by CO and Cl. They were able to investigate the photophysics using the motif of Ir(CO)Cl, which is of great importance to materials research in the field of OLEDs.

In summary, we have presented a new iridium complex with a unique structural motif of a six-membered ring coordinating *via* a methylene group and a pyridine nitrogen atom, and provided reasonable explanations of the nature of the intermediate product and the source of CO insertion. Although possible applications of complex **2** are yet unknown, catalytic activity or data for understanding energy transfer in OLEDs are feasible.

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Notes and references

‡ ^1H NMR (400 MHz, $CDCl_3$, TMS) for **2**: δ(ppm) = 8.77 (d, J = 5.1 Hz, 1H), 8.39 (d, J = 7.8 Hz, 1H), 8.10 (dt, J = 7.8, 7.7, 1.3 Hz, 1H), 7.81 (d, J = 5.9 Hz, 1H), 7.66 (ddd, J = 7.7, 5.1, 1.4 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.37 (t, J = 7.6, 7.6 Hz, 1H), 7.32 (ddd, J = 8.1, 7.5, 1.5 Hz, 1H), 7.23–6.79 (m, br, 6H), 7.08 (ddd, J = 8.1, 1.6, 0.5 Hz, 1H), 6.90 (ddd, J = 7.5, 5.9, 1.6 Hz, 1H), 4.21 (d, J = 10.8 Hz, 1H), 3.76 (d, J = 10.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) for **2**: δ(ppm) = 173.2 (s), 157.9 (s), 156.5 (s), 151.4 (s), 150.7 (s), 150.5 (d), 149.7 (d), 142.3 (s), 141.3 (s), 139.8 (d), 137.7 (d), 136.0 (s), 130.4 (d), 129.5 (d, br), 129.2 (d), 129.2 (d), 128.8 (d), 128.6 (d, br), 128.5 (d), 127.3 (d), 124.9 (d), 123.7 (d), 8.8 (t).

§ Crystal data for **2**: $C_{26}H_{19}Cl_4IrN_2O_3$, M = 741.43, triclinic, a = 11.4605(11) Å, b = 14.1259(14) Å, c = 16.6417(16) Å, α = 89.693(2)°, β = 83.124(2)°, γ = 85.740(2)°, V = 2667.3(4) Å^3, T = 133(2) K, space group $P\bar{1}$, $Z = 4$, $\lambda = 0.71073$ Å, 17162 reflections measured, 17162 unique [R(int) = 0.0000] which were used in all calculations, $R1$ = 0.0425, $wR2$ = 0.1083 ($I > 2\sigma(I)$ for $R1$ and all data for $wR2$).

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