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Title: Electronic effects on the catalytic disproportionation of formic acid to methanol by [Cp*Ir^{III}(R-bpy)Cl]Cl complexes

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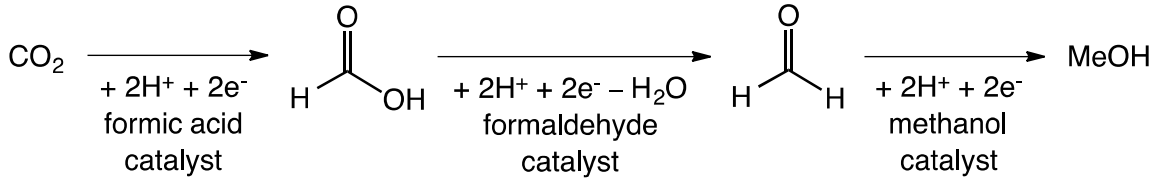
Abstract:

A series of [Cp*Ir^{III}(R-bpy)Cl]Cl (R-bpy = 4,4′-di-R-2,2′-bipyridine; R = CF_3, H, Me, tBu, OMe) complexes was prepared and studied for catalytic formic acid disproportionation. The relationship between the electron donating strength of the bipyridine substituents and methanol production of the corresponding complexes was analyzed; the unsubstituted (R = H) complex was the most selective for methanol formation.

Body:

Most of the world's energy is currently derived from the burning of fossil fuels, which emits carbon dioxide into the atmosphere and contributes to global climate change.[1] In order to continue global modernization in a responsible manner, society is faced with the challenge of further developing clean and sustainable energy technologies. One method of addressing this challenge is to generate fuels from the catalytic reduction of carbon dioxide, thus creating a sustainable carbon-neutral energy cycle.[2] An attractive immediate target product in this endeavor is methanol. Not only is methanol a combustible fuel in itself, it can also be used for the production of electricity by methanol fuel cells and as a feedstock for industrial chemical synthesis, which may one day also rely on renewable carbon sources.[3] However, catalysts capable of transforming carbon dioxide to methanol are rare, and most carbon dioxide reduction or hydrogenation catalysts stop at the level of the two-electron reduction products carbon monoxide or formate.[4] Since the balanced reduction of carbon dioxide to methanol requires six protons and six electrons, it may be difficult for a single molecular catalyst to facilitate the entire transformation. As proposed by Benson, *et al*., utilizing a panel of catalysts, each catalyzing a different step on the reaction pathway from carbon dioxide to methanol (**Scheme 1**), may render the transformation more feasible.[2] The successful application of

a similar approach has been demonstrated recently in the catalytic hydrogenation of carbon dioxide to methanol via formic acid and methyl formate.[5]



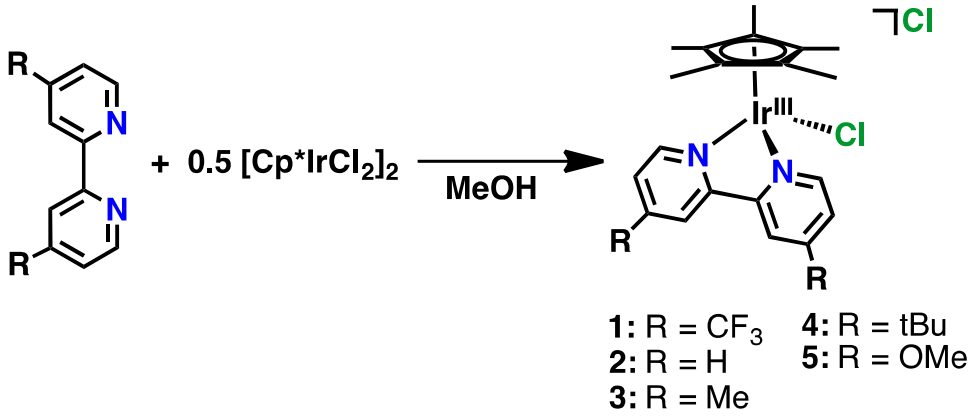
Scheme 1 Proposed scheme for stepwise reduction of carbon dioxide to methanol.

The reductive hydrogenation of carboxylic acids has traditionally required stoichiometric quantities of strong reducing agents. Recently, there have been numerous advancements in the catalytic hydrogenation of carboxylic acids.[6, 7] Amongst these advancements was a breakthrough report of the catalytic disproportionation of formic acid to methanol and carbon dioxide by a known transfer hydrogenation catalyst [(η^5-pentamethylcyclopentadienyl)iridium(2,2′-bipyridine)]$^{2+}$ ([Cp*Ir(bpy)]$^{2+}$).[8] This reaction is formally a transfer hydrogenation with one molecule of formic acid acting as the H_2 donor, releasing CO_2, and another acting as the acceptor, producing formaldehyde. This process is repeated on formaldehyde to generate methanol (**Equations 1-3**). At the time of its publication, this catalyst was the only example of methanol production directly from formic acid and performed with a selectivity of 12% under optimized conditions. The bipyridine ligand of this catalyst provides a convenient handle for modification by facile substitution at the 4 and 4′ positions. The reactivity of this catalyst for ketone transfer hydrogenation and for carbon dioxide and carboxylic acid hydrogenation has been tuned and improved by this method, finding a positive correlation between electron donating strength of the substituent and catalytic activity.[7, 9, 10] Based on those successes, we prepared and evaluated five differently substituted [Cp*Ir^{III}(R-bpy)Cl]Cl complexes (**Scheme 2**) for formic acid disproportionation in order to elucidate the effect of the electron donating strength of the bipyridine substituent on activity and selectivity in an attempt to improve methanol formation.

$$2HCOOH(aq) \longrightarrow CO_2(g) + HCOH(aq) + H_2O(aq) \quad (1)$$

$$HCOOH(aq) + HCOH(aq) \longrightarrow CO_2(g) + CH_3OH(aq) \quad (2)$$

$$3HCOOH(aq) \longrightarrow 2CO_2(g) + CH_3OH(aq) + H_2O(aq) \quad (3)$$



Scheme 2 Preparation of iridium complexes **1**–**5**

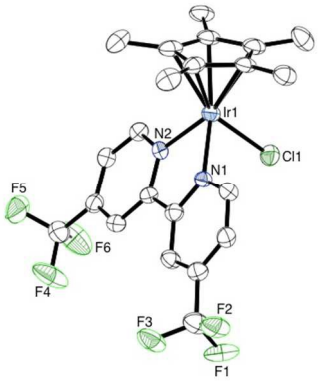


Fig. 1 Thermal ellipsoid plot of the crystal structure of **1** shown at the 50% probability level. Hydrogen atoms, uncoordinated counterions, and solvent molecules are omitted for clarity.

Ir^{III} complexes **1**–**5** were prepared by the reaction of $[Cp^*IrCl_2]_2$ with the corresponding bipyridine ligand in methanol according to previously reported methods[11] and purified as needed with column chromatography and recrystallization. Complexes **1** and **4** are newly reported compounds and were fully characterized by ^1H NMR spectroscopy, X-ray crystallography, and elemental analysis. The characterization data for complexes **2, 3,** and **5** matched previously reported values.[10, 12] Catalytic reactions of each iridium complex were carried out in triplicate. J. Young tubes were charged with solutions of 0.3 mM iridium complex, 3M HCOOH, and 40 mM sodium tosylate in H_2O. Each tube contained a capillary tube of D_2O for locking. The reactions were assessed after 21 hours at 60°C by quantification of methanol and methyl formate, which is

formed from methanol and formic acid, by integration of ^{1}H NMR peaks against a sodium tosylate standard.

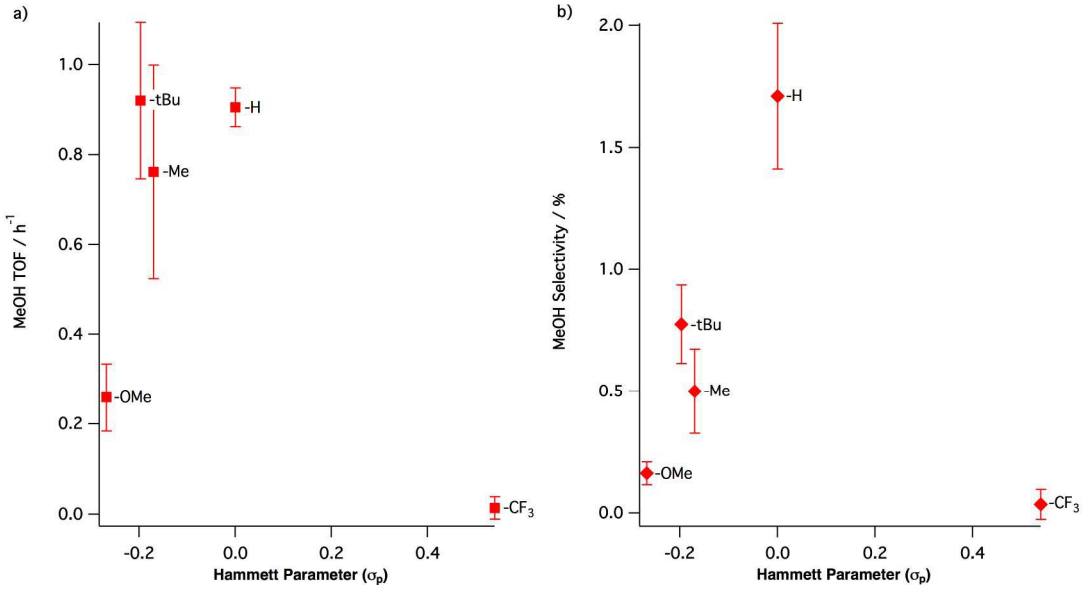


Fig. 2 Catalytic activity for MeOH formation vs. Hammett Parameter for reactions of 0.3 mM iridium complexes with 3M $HCOOH_{aq}$ at 60°C for 21h. (a) TOF at 21h. (b) Methanol selectivity

Turnover frequency and methanol selectivity were calculated according to formulas detailed by Miller, *et al*.[8] Methanol selectivity is a measure of the amount of formic acid that undergoes disproportionation to generate methanol rather than undergoing decomposition to produce side products, mainly hydrogen. See the discussion below for further detail. The Hammett parameter is dependent upon the ratio between the ionization constant of benzoic acid and a substituted benzoic acid and serves as an approximate measure of the relative electron donating strength of said substituent.[13]

Of all the complexes, **4** (R = tBu) demonstrated the highest TOF for methanol formation at 21 hours of 0.92±0.17 h^{-1} (**Table 1**, **Figure 2a**). This was slightly higher than those of **2** (R = H), 0.91±0.04 h^{-1}, and **3** (R = Me), 0.76±0.24 h^{-1}, although the measured performances of the three complexes were equivalent within error. The methanol TOF of the complex substituted with the electron withdrawing trifluoromethyl group (**1**) was 0.01±0.02 h^{-1}. This was expected due to the previously demonstrated detrimental effect of electron withdrawing substituents on catalytic activity for ketone transfer hydrogenation and carbon dioxide reduction.[9, 10] The complex with the most electron donating substituent, **5** (R = OMe), displayed a methanol TOF of 0.26±0.07 h^{-1},

lower than **2–4**. Therefore, contrary to the cases of ketone transfer hydrogenation and carbon dioxide transfer hydrogenation, substitution on the bipyridine ligand with electron donating groups did not improve the TOF for formic acid disproportionation.

For methanol selectivity, complex **2** was the highest of those examined (1.17±0.30 %), with both electron donating and electron withdrawing groups having an adverse effect on selectivity. The complexes substituted with electron donating alkyl groups, **3** and **4**, performed more poorly than the unsubstituted complex **2** in terms of methanol selectivity, unlike with methanol TOF, where the three complexes performed equivalently.

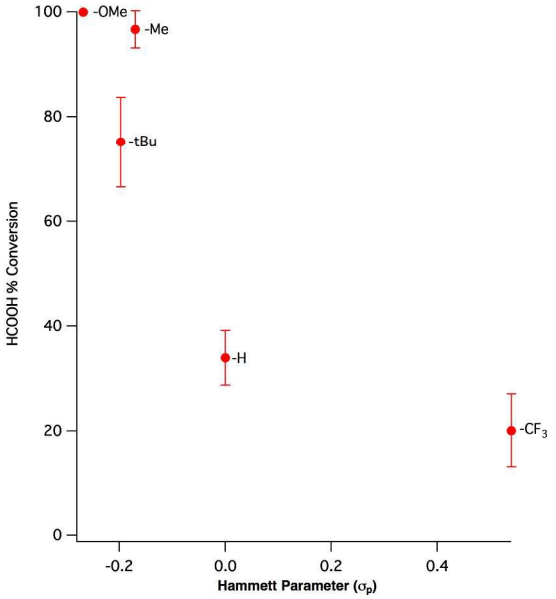


Fig. 3 Formic acid conversion vs. Hammett Parameter for reactions of 0.3 mM iridium complexes with 3M $HCOOH_{aq}$ at 60°C for 21h

Complex	R group	Hammett parameter (σ_p)	TOF (h^{-1})	MeOH selectivity (%)	HCOOH conversion (%)
1	CF_3	0.540	0.01±0.02	0.04±0.06	20.0±7.0
2	H	0	0.91±0.04	1.17±0.30	33.9±5.2
3	Me	-0.170	0.76±0.24	0.50±0.17	96.7±3.5
4	tBu	-0.197	0.92±0.17	0.77±0.16	75.2±8.6
5	OMe	-0.268	0.26±0.07	0.16±0.05	99.9±0.0

Table 1 TOF, MeOH selectivity, and HCOOH conversion of **1–5**

Analyzing the results in terms of formic acid conversion (**Figure 3**), also detailed by Miller, *et al*.,[8] it is evident that there is a correlation between the electron donating power of the bipyridine substituent and the quantity of formic acid consumed in the reaction. This is consistent with the observation that **3** and **4** had decidedly lower selectivities than **2** even though they had roughly the same TOF. In effect, while the complexes with the more electron donating substituents consume formic acid more rapidly, they do not necessarily transform it into methanol more efficiently. The most likely explanation for this observation is that the extra electron donation simply drives the decomposition of formic acid into hydrogen and carbon dioxide to proceed more quickly, thus outcompeting the formation of methanol. This would be consistent with the reaction scheme proposed by Miller, *et al*.,[8] where reaction of the iridium complex with one equivalent of formic acid forms the catalytically active hydrido species, $[Cp^*Ir(bpy)H]^+$, which then reacts, presumably by outer sphere hydride transfer, with further equivalents of formic acid, possibly protonated, to afford methanol or with a proton to form hydrogen. In this scenario, a more strongly donating ligand would not be predicted to make the catalyst favor reaction with formic acid to form methanol over hydrogen even if the resulting hydride is stronger. Additionally, if the key reaction is indeed between $[Cp^*Ir(bpy)H]^+$ and protonated formic acid, the formation of protonated formic acid may be involved in the rate limiting step and thus, additional hydride strength would not necessarily affect the rate of methanol formation, and would accelerate the formation of hydrogen.

While increasing electron donation from the bipyridine substituent increased rates of ketone transfer hydrogenation with this catalyst, catalysis of formic acid disproportionation did not follow the same trend.[9] One plausible explanation for this is that the yields and rates of ketone transfer hydrogenation reactions do not account for the total quantity of formic acid consumed. Therefore, a low selectivity could go unnoticed. An additional advantage in the transfer hydrogenation of ketones over that of formic acid, along with the inherently higher reactivity of ketones in general, is that ketone transfer hydrogenation can operate at higher pH values, thus disfavoring hydrogen production, whereas high concentrations of formic acid are preferred for formic acid disproportionation and no increase in selectivity was seen at higher pH values.[8]

Conclusions:

In summary, a series of five [Cp*Ir^{III}(R-bpy)Cl]Cl complexes were prepared and compared for formic acid disproportionation catalysis. The most proficient complex in terms of methanol selectivity was the unsubstituted bipyridine complex **2**. In terms of rate of methanol formation, **2** and **4** were the most active complexes, equivalent to each other within error.

Some important lessons to guide further study in the catalytic generation of methanol can be drawn from this work. The fact that increasing electron donation from the bipyridine ligand does not improve these complexes for formic acid disproportionation as it did with CO_2 hydrogenation is noted. The hydrogenation of CO_2 into formate proceeds under basic conditions, while the hydrogenation of formic acid into methanol requires acidic conditions. The protons at low pH can also react with the hydrido catalyst complex to generate hydrogen. Work aiming to produce methanol from CO_2 must take into account the careful balance of electron donating strength and proton concentration required for each step of the transformation.

Recently there have been reports of formic acid disproportionation with molybdenum and ruthenium catalysts, which demonstrated improved selectivities for methanol formation of up to 21% and 50.2 % respectively.[14, 15] A key difference between the iridium complexes presented here and the ruthenium triphos catalyst, the most selective of all the examples, is that the ruthenium triphos catalyst has multiple open coordination sites for the binding of further equivalents of formic acid. This could encourage inner sphere hydride transfer to formic acid over transfer to a proton to generate hydrogen and thus increase selectivity. Designing new catalysts that can hydrogenate formic acid by inner sphere mechanisms may provide a viable route to methanol from formic acid.

Acknowledgements:

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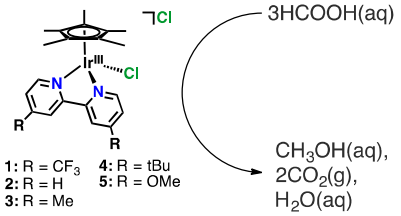

The electronic effects on the catalytic disproportionation of formic acid to methanol by a series of iridium complexes are elucidated.