

COMMUNICATION

THE SYNTHESIS OF ORGANO-IMIDO COMPLEXES OF Cr(IV) AND Fe(III)

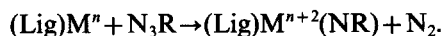
ROBYN L. ELLIOTT, PETER J. NICHOLS and BRUCE O. WEST*

Department of Chemistry, Monash University, Clayton, Victoria 3168, Australia

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Abstract—The reaction of *p*-tolylazide with (5,10,15,20-tetraphenylporphyrinato) chromium(II) (Cr(TPP)) yields the high spin chromium(IV) organo-imido complex, $\text{CH}_3\text{C}_6\text{H}_4\text{N}=\text{Cr}(\text{TPP})$. *N,N'*-ethylene-bis-(salicylideneiminato)iron(II), (Fe(salen)), however reacts with arylazides to produce iron(III) organo-imido-bridged compounds of general formula, $[\text{Fe}(\text{salen})]_2\text{NR}$ showing magnetic coupling between the Fe(III) centres.

The synthesis and study of transition metal organo-imido complexes ($\text{M}=\text{NR}$) is of considerable current interest.¹ However, relatively few examples are yet known of compounds in which chelating ligands are attached to the metal in addition to the organo-imido group.^{2–5} One synthetic route which seems to have potential application to a wide variety of metals involves reaction between arylazides and metal chelate complexes which are readily oxidizable by a two electron process to give the organo-imide with nitrogen as the second product thus,



This type of reaction has been used with particular success in synthesizing $(\text{Lig})_2\text{Mo}(\text{VI})(\text{NR})_2$ complexes from $\text{Mo}(\text{II})$ ^{3,4} and $\text{Mo}(\text{IV})$ ⁵ starting materials with Lig = dithiocarbamate or dithiophosphato ligands.

We wish to report the synthesis of the first chromium porphyrin organo-imido complex, *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{N}=\text{Cr}(\text{TPP})$ by reaction of the air sensitive metalloporphyrin, Cr(II)(TPP), with excess *p*-tolylazide in toluene with rigorous exclusion of moisture and air. When solutions of the reagents are mixed at room temperature, a gradual change in colour is observed over 10 min from the brown

of Cr(II)(TPP) to the green-brown solution containing the product. Nitrogen is evolved during the reaction. The complex is precipitated as a green-brown solid by addition of hexane.

The molecular ion $[\text{CH}_3\text{C}_6\text{H}_4\text{N} \cdot \text{Cr}(\text{TPP})]^{++}$ is observed as a low intensity peak in the mass spectrum of the compound together with $[\text{Cr}(\text{TPP})]^{++}$ and $[\text{CH}_3\text{C}_6\text{H}_4\text{NH}]^+$, the latter peak being particularly intense. Elemental microanalyses and mass spectroscopy indicate the presence of one further molecule of toluene in the product. The magnetic moment for the complex in the solid state at 293K is 2.7 BM, consistent with a spin free d^2 , Cr(IV) system. This may be compared with the diamagnetism (or at least very low paramagnetism) found for a variety of Cr(IV) oxo porphyrin⁶($\text{O}=\text{Cr}(\text{IV})(\text{P})$) derivatives, including the isoelectronic $\text{O}=\text{Cr}(\text{TPP})$.

The UV/visible spectrum of the complex in toluene displays a Soret band at 423 nm with a further low intensity band at 537 nm. $\text{O}=\text{Cr}(\text{TPP})$ has similar bands at 431 and 544 nm.⁶ Addition of tetrahydrofuran (THF) or *N*-methylimidazole (*N*-MeIm) causes shifts in the position of the Soret band and the appearance of several new bands at higher wavelengths, indicating coordination of these donor molecules to the Cr atom in the organo-imido complex thus†

THF/toluene λ_{max} = 410sh, 433, 555, 594 nm

N-MeIm/toluene λ_{max} = 417sh, 439, 558, 604 nm.

Tetrahydrofuran binds notably more strongly to the organo-imido complex than to $\text{O}=\text{Cr}(\text{TPP})$

*Author to whom correspondence should be addressed.

†The determination of accurate extinction coefficients has been found to be very difficult because of the combination of low solubility and sensitivity to moisture of this complex.

since the addition of comparable amounts of THF to a toluene solution of $\text{O}=\text{Cr}(\text{TPP})$ causes no change in position or intensity of the absorption maxima.

It has not been possible to determine unambiguously a value for the $\text{Cr}-\text{N}(\text{imido})$ stretching frequency in this complex because of the multitude of ligand vibrations in the $850\text{--}1150\text{ cm}^{-1}$ region where the frequency may be expected.⁷

The complex reacts with PPh_3 in toluene yielding the phosphine-imide $\text{CH}_3\text{C}_6\text{H}_4\text{N}=\text{PPh}_3$, this product being identified by its mass spectrum after evaporation of the reaction mixture under vacuum and extraction of the phosphine-imide together with excess PPh_3 by hexane. $\text{Cr}(\text{II})(\text{TPP})$, the second product formed, was detected in the reaction mixture by its characteristic Soret absorption band at 421 nm .⁶ Oxygen transfer from $\text{O}=\text{Cr}(\text{TPP})$ to PPh_3 has been shown to occur readily.⁸

We have also observed that the readily oxidised complex, $\text{Fe}(\text{II})(\text{salen})$, undergoes smooth reactions at room temperature with a variety of arylazides.

Thus, when $\text{Fe}(\text{salen})$ reacted with *p*-tolylazide in dry CH_2Cl_2 under nitrogen the initial red-brown colour of the mixture lightened rapidly and nitrogen was evolved. Addition of hexane precipitated a black, microcrystalline complex whose microanalysis indicated a solvated product of formula $[\text{Fe}(\text{salen})]_2\text{NC}_6\text{H}_4\text{CH}_3 \cdot \text{CH}_2\text{Cl}_2$. The mass spectrum of the product does not display the molecular ion of the complex but peaks due to $[\text{Fe}(\text{salen})]^{+}$ and $[\text{CH}_3\text{C}_6\text{H}_4\text{NH}]^{+}$ were dominant once the very volatile CH_2Cl_2 had been removed. The compound has a magnetic moment $\mu_{\text{eff}} = 2.8\text{ BM}$ per dimer at 293 K similar to that found for the μ -oxo derivative⁹ ($\mu_{\text{eff}} = 2.7\text{ BM}$). Solutions of the complex in CH_2Cl_2 rapidly turn orange in colour when exposed to air due to the formation of an $\text{Fe}(\text{III})(\text{salen})$ hydrolysis product while *p*-toluidine is also recovered. The complex does not react with triphenylphosphine.

Unsolvated complexes have been isolated from toluene solution using *p*-tolyl, *p*-chloro and phenylazides. Their general properties and magnetism, each similar to those described for the CH_2Cl_2 solvated *p*-tolyl derivative, strongly indicate that they

are organo-imido bridged derivatives as in (a). The reduced magnetic moments observed for these complexes are no doubt due to extensive spin-coupling through the organo-imido bridge as found for the complexes $[\text{Fe}(\text{III})(\text{salen})]_2\text{X}$, $\text{X} = \text{O}^9$ and S .¹⁰ Detailed magnetic studies on several of the complexes will be reported elsewhere.

A number of homobinuclear^{1,11} and trinuclear^{12,13} bridged organo-imido derivatives have been reported with carbonyl or cyclopentadienyl groups attached to the metal. The present iron complexes appear to be the first examples of organo-imido bridged compounds involving simple chelating ligands.

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