

quired. Consequently, 2-DMNO was irradiated in three solutions: methanol, 0.5 M acetic acid in methanol, and 0.5 M KOH in methanol. The same products were formed 1.3 times faster in the acid solution compared to the other two as shown by uv analysis of the reaction mixture at 347 nm, a naphthylamine chromophore. Though the rate difference is not great, this indicates that $O^{\cdot-}$ is first formed which, with its respectable basicity ($pK_a = 11.9$), protonates shortly thereafter.

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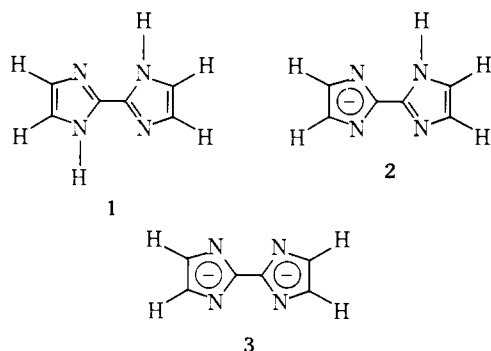
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Rhodium(I) and Iridium(I) Complexes of Anions of 2,2'-Biimidazole

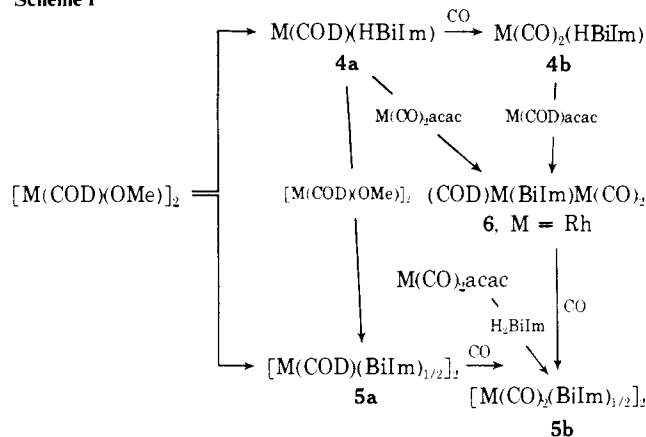
Sir:

Organic and inorganic substances which possess highly anisotropic conduction, dielectric, and optical properties arise from the crystallization of planar, sterically compact molecules or ions which possess delocalized electrons and accessible, stable oxidation states. Examples of organic materials are the salts of tetracyanoquinodimethan (TCNQ)¹ and salts of tetrathiofulvalene (TTF).² Inorganic salts are typified by the platinum mixed-valence salt $K_2Pt(CN)_4Br_{0.3} \cdot 3H_2O$ ³ and the iridium complex $Ir(CO)_3Cl_{1.1}$.⁴ These materials and their properties have been reviewed.⁵

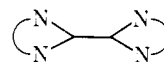
The purpose of this study was to explore combinations of compact delocalized ligands and 4d and 5d transition metals in an effort to obtain new materials which may possess unusual physico-chemical properties. This communication describes the synthesis and characterization of new rhodium(I) and iridium(I) complexes derived from the conjugated ligand 2,2'-biimidazole (H_2BiIm), **1**.



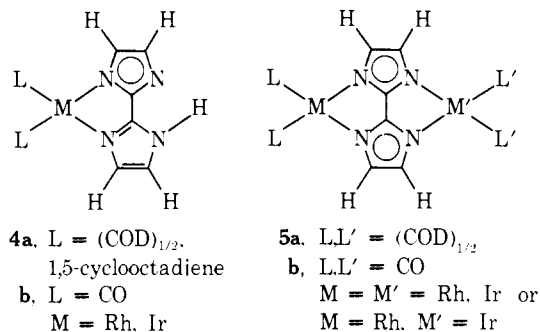
Scheme I



The coordination properties of H_2BiIm and its anionic derivatives, **2** and **3**, have not been thoroughly examined. Since the synthesis of H_2BiIm in 1859 by Debus,⁶ only complexes of Cu(II),⁷ Ni(II),^{7,8} Co(II),⁷ and Fe(II)⁷ which contain coordinated neutral biimidazole have been prepared. The coordination geometry of the nickel complex $[Ni(H_2BiIm)_2(H_2O)_2](NO_3)_2$ has been determined by an X-ray crystallographic study.⁸ The addition of hydroxide ion to aqueous solutions of these complexes resulted in the precipitation of insoluble complexes believed to contain the monoanion $HBiIm$, **2**.⁷ The syntheses described below result in tractable mononuclear products of the $HBiIm$ and homo- and heterodinuclear products of the hitherto unknown dianion $BiIm$, **3**. We believe the latter products represent the first examples of dinuclear complexes containing the tetracoordinate bisamidine or tetraza linkage



The selective production of derivatives of **2** and **3** is illustrated in Scheme I.⁹ The reactions are driven by the use of strong bases¹⁰ OMe^- and $acac^-$ ($acac^-$ = acetylacetonate ion). The rhodium and iridium complexes abstract a pyrrole proton from H_2BiIm forming the homogeneous reaction product $MeOH$ or $Hacac$.¹¹ The reactions were carried out under argon in dry, deaerated solvents with nearly quantitative yields.



Bright yellow crystals of air stable $Rh(COD)(HBiIm)$, **4a**, are obtained by treating $[Rh(COD)(OMe)]_2$ with 2 mol of H_2BiIm in refluxing methylene chloride for 30 min. Lustrous orange needles of air stable $Rh(CO)_2(HBiIm)$, **4b**, form when carbon monoxide is passed through a benzene solution of **4a** readily displacing the diene. The corresponding **4a** and **4b** (M = Ir) are light orange and black, respectively, and are air stable. Two infrared carbonyl absorptions in solutions of **4b** (M = Rh 2079 (s), 2011 (s); M = Ir 2068 (s), 2000 (s)) are consistent with a *cis* dicarbonyl structure.

The homodinuclear complexes, **5a**, can be prepared as in the method above by adjusting the mole ratio to 1:1. Complexes, **5b**, are obtained through *in situ* displacement of COD from **5a** by carbon monoxide.¹² Dimers, **5b**, may be prepared by the stoichiometric reaction of $M(\text{CO})_2\text{acac}$ with H_2BiIm . However, unlike reactions with $[M(\text{CO-D})(\text{OMe})]_2$ only dimeric species are obtained regardless of molar ratios. The ir spectrum (CH_2Cl_2 solution, cm^{-1}) of **5b** ($M = \text{Rh}$) contains four CO stretching bands at 2095 (m), 2081 (s), 2026 (m), and 2014 (m); this is indicative of a solution species with symmetry lowered from that for a totally symmetric molecule (D_{2h} with two ir active stretching modes). The spectrum of **5b** ($M = \text{Rh}$) labeled with 90% ^{13}C likewise contains four bands shifted as expected to 2046 (m), 2032 (s), 1980 (m), and 1968 (m). Complexes **5a**, bright yellow ($M = \text{Rh}$) and red-orange ($M = \text{Ir}$), and **5b**, dark red ($M = \text{Rh}$), are air and solution stable, whereas the deep purple **5b** ($M = \text{Ir}$) is not air stable. H_2BiIm may be recovered quantitatively and unaltered from **5** by reaction with HCl .¹³ No N-H infrared absorption modes, as identified in the ir spectra of complexes containing H_2BiIm , are observed in the spectra of **5a** and **5b** indicating that the ligand is the dianion BiIm^- .

Since each of the mononuclear derivatives **4** contains one reactive pyrrole hydrogen, it may be considered an intermediate in dimer formation. Thus, **5a** may be prepared from **4a** by the reaction of **4a** and $[M(\text{COD}(\text{OMe}))_2]$ (Scheme I). The mixed ligand homodinuclear complex **6** may be obtained through the reaction of RhL_2acac and the appropriate mononuclear derivative **4**.¹⁴ The complete series of heterodinuclear derivatives $\text{L}_2\text{M}(\text{BiIm})\text{M}'\text{L}'_2$, where L_2 and L'_2 may be identical, is readily prepared through suitable combinations of **4a** or **4b** and $\text{M}'\text{L}'_2\text{acac}$. The use of the mononuclear derivatives as intermediates for the incorporation of other metals is under investigation.

The nmr spectra of complexes **5a** and **5b** ($M = \text{Rh}$) revealed unexpected solvent-dependent behavior. The ^1H nmr spectrum of **5a** contained a single resonance (for example, δ (CDCl_3) 6.38; δ (CCl_4) 6.21) assigned to chemically equivalent biimidazole ring hydrogens¹⁵ of a symmetrical dinuclear structure **5a**. For the tetracarbonyl derivative **5b** again one resonance was observed (δ 6.58) when the solvent was either C_6D_6 or $\text{C}_6\text{D}_5\text{CD}_3$; however, two peaks of equal area appeared when other solvents were used (for example, δ (CDCl_3) 6.88, 6.77; δ (CCl_4) 6.83, 6.67; δ (CD_3COCD_3) 7.00, 6.94). These resonances are due to chemically shifted protons as confirmed by spectra at both 60 and 100 MHz. Stepwise addition of CDCl_3 to a C_6D_6 solution of **5b** resulted in initial broadening of the single resonance followed by separation into two resonances of equal area. Temperature-dependent studies in CDCl_3 from -55 to $+60^\circ$ and in $\text{C}_6\text{D}_5\text{NO}_2$ (δ 7.00, 6.86) from 25 to 110° indicate stereochemical rigidity over that temperature range. For iridium complexes **5a** and **5b**, two resonances, chemically shifted, are observed for the ring hydrogens independent of solvent. The ^{13}C nmr spectrum of **5b** ($M = \text{Rh}$) in toluene and chloroform contained two overlapping doublets of approximately the same chemical shift (δ ($\text{C}_6\text{D}_5\text{CD}_3$) = 187.56, 186.55; δ (CDCl_3) 186.32, 185.02; both relative to TMS) and intensity with $J_{\text{Rh-C}} = 65-70$ Hz. These chemical shifts and coupling constants are in the range expected for terminal Rh-CO species.¹⁶ Although the specific origin of the different chemical shifts has not been determined, the data indicate the presence of an unsymmetrical solution species which may be due to solvent association.

The methods described herein provide routes for the selective preparation of a wide variety of complexes containing anionic biimidazolates. Oxidation studies of all complexes and X-ray crystal structure determinations on

$[\text{Rh}(\text{CO})_2(\text{BiIm})_{1/2}]_2$ and $[\text{Rh}(\text{COD})(\text{BiIm})_{1/2}]_2$ are in progress.

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- (10) No acid dissociation of H_2BiIm is observed to a pH of 11.5; ref. 7.
- (11) Reactions with chloro-bridged metal complexes resulted in low yields possibly due to reprotonation and subsequent generation of uncharacterized side products.
- (12) The quantitative determination of molar uptake of carbon monoxide is 4.16 to 1 for this reaction as compared with the theoretical ratio of 4 to 1.
- (13) Rather than adding oxidatively, HCl cleaves the dimer to form protonated H_2BiIm and chloro-bridged complexes $[\text{ML}_2\text{Cl}]_2$. The neutral ligand H_2BiIm is recovered through the addition of Na_2CO_3 to an aqueous solution of the ligand salt.
- (14) Reactions of equimolar rhodium and iridium reagents with H_2BiIm have produced mixtures of homo- and heterodinuclear complexes.
- (15) Integration of peak ratios revealed the expected 4:1 COD to BiIm proton ratio.
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Metallocarborane Complexes of Titanium, Zirconium, and Vanadium

Sir:

The cyclopentadienyl organometallic chemistry of the group IV and V transition metals has now been well established,¹ and, although the stabilizing influence exerted by a carboranyl ligand as compared to a cyclopentadienyl ligand is also well known,² metallocarborane complexes of these metals have heretofore escaped synthesis. We now report the first metallocarboranes of the early transition metals titanium, zirconium, and vanadium with the observation that their stabilities considerably exceed those of the corresponding cyclopentadienyl analogs.

The reduction of closo carboranes ($\text{C}_2\text{B}_n\text{H}_{n+2}$) with 2 equiv of sodium followed by complexation with various transition metals to yield $(n+3)$ vertex metallocarboranes has been accomplished.³ We have found that the dianion generated from $1,2\text{-C}_2\text{R}_2\text{B}_{10}\text{H}_{10}$ ($\text{R} = \text{H}, \text{Me}$) reacts with the metal halides TiCl_4 , ZrCl_4 , and VCl_3 to generate a series of anionic metallocarboranes formulated as $[\text{M}(\text{C}_2\text{R}_2\text{B}_{10}\text{H}_{10})_2]^{2-}$ with M in the formal +2 oxidation state ($\text{M} = \text{Ti}, \text{R} = \text{H}, \text{Me}; \text{M} = \text{Zr}, \text{R} = \text{Me}; \text{M} = \text{V}, \text{R} = \text{H}$) and isolable in good yield (60-75%) as tetraalkylammonium salts.⁴