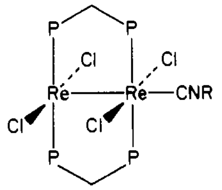
the electrochemical and redox characteristics of **2** strongly support the presence of multiple metal–metal bond character. Since **2** is diamagnetic, a formal Re–Re bond order of at least 2 is implied.

The isolation and structural identification of **2** provides insights into the intermediates that are formed when isocyanide ligands cleave M–M multiple bonds. In the solid state, structure **2** is apparently more stable than the alternative one **3**, which we can envisage as representing the species that is formed upon the initial interaction of isocyanide with **1**. The rearrangement **3** → **2** is clearly favored in this system.

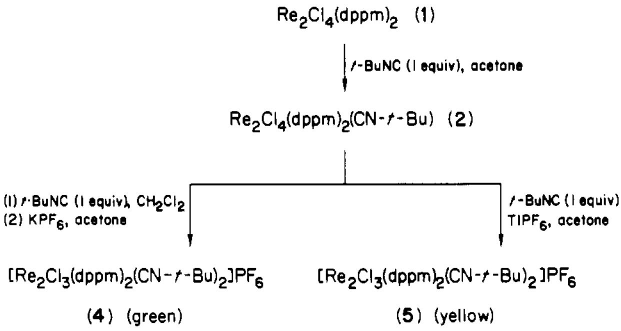


3 (P⌒P = dppm, R = *t*-Bu)

The corresponding reactions of $Re_2Cl_4(LL)_2$, where LL = dppe, arphos,[18,19] with *t*-BuNC are very sluggish, due to the limited solubility of these complexes in the reaction solvents. However, their much more soluble oxidized congeners $[Re_2X_4(LL)_2]PF_6$ (X = Cl, Br; LL = dppe, arphos)[20] react smoothly when treated with the isocyanide ligands *t*-BuNC and *i*-PrNC (2–4 equiv) in CH_2Cl_2 to give the dirhenium(II) complexes $[Re_2X_3(LL)_2(CNR)]PF_6$ in ca. 75% yield (based on starting complex).[21] Each of these green to brown solids behaves as a 1:1 electrolyte in acetone and exhibits a single, sharp IR-active $\nu(C\equiv N)$ mode (2141–2155 cm^{-1}). They possess similar electrochemical properties, with a reversible oxidation at $E_{1/2}$ = ca. +0.65 V and an irreversible reduction at $E_{p,c}$ = ca. −1.5 V vs. SCE. The ^1H NMR spectra of these complexes are consistent with their formulation as diamagnetic, triply bonded Re_2^{4+} species containing a single isocyanide ligand. They most likely possess a staggered structure similar to that of the parent $Re_2X_4(LL)_2$ complexes.[19]

While the complexes $[Re_2X_3(LL)_2(CNR)]PF_6$ (X = Cl, Br; R = *i*-Pr, *t*-Bu; LL = dppe, arphos) are quite inert to further reaction with RNC, the same is not true of $Re_2Cl_4(dppm)_2$(CN-*t*-Bu). In this instance, the treatment of **2** with 1 equiv of *t*-BuNC, or of **1** with 2 equiv of this same ligand, gives diamagnetic complexes of stoichiometry $[Re_2Cl_3(dppm)_2$(CN-*t*-Bu)$_2]PF_6$ (**4** and **5**) as shown in Scheme I.[22] The formation of **5** is favored by the presence of $TlPF_6$; this reagent apparently labilizes one of the Re–Cl bonds (leading to the precipitation of TlCl) prior to the attack of the second molecule of *t*-BuNC. While we believe that **4** and **5** may be structural isomers, we have not as yet been able to convert one to the other. Both complexes behave as 1:1 electrolytes in acetone (Λ_m = 100–120 Ω^{-1} cm^2 mol^{-1} for $c_m = 1 \times 10^{-3}$ M), and they exhibit distinctly different spectral properties. Their IR spectra show only terminal $\nu(C\equiv N)$ modes,[23] while in the $^{31}P\{^1H\}$ NMR spectra an AA′BB′ pattern is observed for **4**, whereas an AA′XX′ pattern is found for complex **5**.[23] These data support the notion that in both **4** and **5** the two dppm ligands retain their trans-bridging disposition. The ^1H NMR spectrum of **4** (recorded in CD_2Cl_2) exhibits only one resonance for the isocyanide ligands (δ = +0.68), indicating that both isocyanides are magnetically equivalent, and a pentet (δ = +6.00, J_{PH} = 5.3 Hz) associated with the methylene protons of the dppm ligands. This constitutes good evidence that **4** does *not* possess an A-frame type structure.[7] Its structure is, we believe, closely akin to that of the recently characterized triply bonded nitrile derivatives $[(RCN)_2ClRe(\mu\text{-dppm})_2ReCl_2]X$ (R = Me, Et, Ph, 4-Ph-C_6H_4; X = Cl^-, PF_6^-).[24] This is supported by the striking similarity of the electrochemical properties of **4** and the nitrile-containing complexes.[25] Complex **5** shows an AB pattern in the ^1H NMR spectrum (δ_A = +6.00; δ_B = +5.42), and as for complex **2**, an A-frame structure may be present. The ^1H NMR spectrum of **5** also exhibits two resonances for the isocyanide ligands (δ = +2.03 and +1.24), thereby showing that the two isocyanide ligands are inequivalent.

Scheme I. Reactions of $Re_2Cl_4(dppm)_2$ with *tert*-Butyl Isocyanide



Work is under way to expand the scope of these studies to include reactions of isocyanides with other complexes of the type $M_2X_4(dppm)_2$ (M = Mo, W, Re; X = Cl, Br). Full details will be published following completion of structural studies.[26]

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(18) Ebner, J. R.; Tyler, D. R.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 833.

(19) Cotton, F. A.; Stanley, G. G.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2099.

(20) Brant, P.; Glicksman, H. D.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 3203.

(21) Satisfactory elemental microanalyses were obtained for all six complexes of this type. For example: Anal. Calcd for $[Re_2Cl_3(dppe)_2$(CN-*t*-Bu)$]PF_6$: C, 45.51; H, 3.83. Found: C, 45.12; H, 4.08.

(22) Anal. Calcd for $C_{60}H_{62}Cl_3F_6N_2P_5Re_2$: C, 46.23; H, 4.01; Cl, 6.82. Found (**4**): C, 45.78; H, 3.94; Cl, 6.99. Found (**5**): C, 45.49; H, 3.83; Cl, 6.51.

(23) Complex **4**: IR (Nujol) $\nu(C\equiv N)$ 2186 w, 2159 s, 2127 sh cm^{-1}; IR (CH_2Cl_2) $\nu(C\equiv N)$ 2188 w, 2164 s, 2124 w cm^{-1}; $^{31}P\{^1H\}$ NMR (H_3PO_4 external, 3:1 CH_2Cl_2–acetone-d_6) δ_A = −10.71, δ_B = −15.15, $J_{AA'}$ = 198.8 Hz, $J_{BB'}$ = 178.5 Hz, J_{AB} = 78.5 Hz, $J_{AB'}$ = 2.6 Hz. Complex **5**: IR (Nujol) $\nu(C\equiv N)$ 2138 sh, 2124 s cm^{-1}; IR (CH_2Cl_2) $\nu(C\equiv N)$ 2140 sh, 2125 s cm^{-1}; $^{31}P\{^1H\}$ NMR (H_3PO_4 external, 3:1 CH_2Cl_2–acetone-d_6) δ_A = +5.08, δ_B = −13.35, $J_{AA'}$ = 162.2 Hz, $J_{BB'}$ = 130.4 Hz, J_{AB} = 61.7 Hz, $J_{AB'}$ = 7.7 Hz.

(24) Barder, T. J.; Cotton, F. A.; Falvello, L. R.; Walton, R. A. *Inorg. Chem.*, in press.

(25) Solutions of **4** in 0.2 M Bu_4NPF_6–CH_2Cl_2 are characterized by a one-electron oxidation at $E_{1/2}$ = +0.65 V vs. SCE and an irreversible reduction process at ca. −1.6 V vs. SCE. The corresponding processes for **5** are an oxidation at +1.04 V and an irreversible reduction at $E_{p,c}$ = −1.07 V vs. SCE.

(26) Support from the National Science Foundation (Grant No. CHE82-06117) is gratefully acknowledged.

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Received October 16, 1984

Homogeneous Models for Propylene Ammoxidation. 2. The Carbon–Nitrogen Bond-Forming Step[1]

Sir:

The ammoxidation of propylene is a major industrial process by which 8 billion pounds of acrylonitrile are produced annually. In this process, a mixture of propylene, ammonia, and air is passed over a heterogeneous bismuth molybdate-containing catalyst (eq 1).

$$CH_2{=}CHCH_3 + NH_3 + {}^3/{}_2O_2 \xrightarrow[400\ ^\circ C]{Bi_2O_3/MoO_3} CH_2{=}CHCN + 3H_2O \quad (1)$$

The rate-limiting step for eq 1 is C–H bond cleavage to produce

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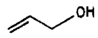
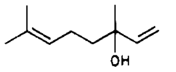
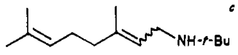
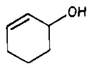
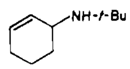
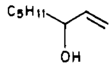
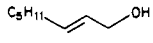
(1) Part 1: Chan, D. M.-T.; Fultz, W. C.; Nugent, W. A.; Roe, D. C.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 251–252.

Table I. Products from Peroxide-Initiated Reaction of Imido Complexes with Toluene[a]

imido complex	amt of benzoyl peroxide, mmol	amt of products,[b] mmol			imido complex	amt of benzoyl peroxide, mmol	amt of products,[b] mmol		
		3	phenyl toluenes[c]	bibenzyl			**3**	phenyl toluenes[c]	bibenzyl
2a	0.50	0.34	0.23	0.03	$(Me_3SiO)_2CrO(N\text{-}t\text{-}Bu)$	1.0	0.52	0.40	<0.01
2a	1.0	0.43	0.40	0.04	**2b**	1.0	0.07	0.22	0.05
2a	1.5	0.48	0.60	0.07	none	1.0	0.00	0.55	0.22
2a	none	<0.01	<0.01	<0.01					

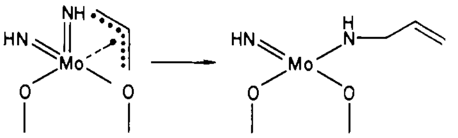
[a] All runs contained 1 mmol of imido complex in 10 mL of toluene (100 °C, 16 h). [b] Capillary GC yields vs. internal standard tridecane. [c] As mixture of ortho, meta, and para isomers; see text.

Table II. Allylic Amines from Reaction of Allylic Alcohols with **5**[a]

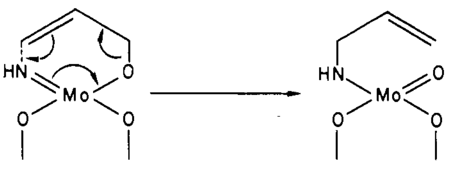
entry	alcohol	solvent	temp, °C	time, h	product	yield,[b] %
1		mesitylene	146	68		60
		toluene	110	68	 [c]	90
3		toluene	110	18		36
4		toluene	110	108	 [d]	82
5		mesitylene	150	168		19

[a] Reactions using 1:1.1 alcohol:**5** ratio under nitrogen in specified solvent (0.5 M concentration). [b] All are isolated yields except the yield of entry 1, which was determined by GC. [c] Isomeric *E*:*Z* = 1:1. [d] Isomeric *E*:*Z* = 4:1.

a symmetrical allyl moiety[2] (presumably an adsorbed allyl radical).[3] The critical C–N bond-forming step is much less well understood. However, on the basis of recent studies on heterogeneous systems by Grasselli et al.,[4] two distinct pathways may be envisioned: (1) direct trapping of the allyl radical at molybdenum diimido sites (eq 2); (2) initial trapping of the allyl radical



(2)



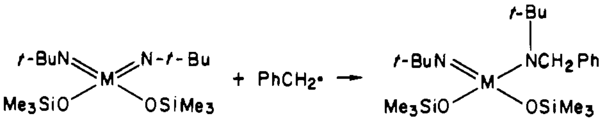
(3)

at a molybdenum oxo group followed by allyl migration from oxygen to an imido nitrogen atom (eq 3). Neither of these reactions has direct precedent in homogeneous systems.[5,6]

For our studies, diimido complexes **2**[7] were selected as models for the postulated active sites in ammoxidation. Benzyl rather than allyl radicals were chosen for study since the products of allyl radical oxidation are not expected to be stable under our reaction conditions and because benzyl and allyl exhibit similar behavior in oxidation reactions.[8] When a solution of **2a** in toluene was heated at 100 °C in the presence of benzoyl peroxide as a radical initiator, benzylidene-*tert*-butylamine (**3**) was obtained in up to 52% yield (Table I). The remaining organic products were CO_2,[9] bibenzyl, and the expected[10] isomeric distribution (ortho:meta:para = 63:21:16) of methylbiphenyls. Thus, we propose that initiator-derived (eq 4) phenyl radicals abstract benzylic hydrogen from toluene to produce benzyl radicals (eq 5).

$$(PhCO_2\text{–})_2 \rightarrow 2Ph\cdot + 2CO_2 \tag{4}$$

$$Ph\cdot + PhCH_3 \rightarrow Ph\text{–}H + PhCH_2\cdot \tag{5}$$



(6)

2a, M = Cr
b, M = Mo

4

$$\mathbf{4} \xrightarrow{-H^+} PhCH{=}N\text{-}t\text{-}Bu \tag{7}$$

The high yields of **3** suggest that benzyl radicals are efficiently trapped and oxidized by **2a**, presumably with intermediate formation of chromium(V) amido complex **4** (eq 6). Apparently the amide ligand of **4** is further oxidized to the Schiff base **3** (eq 7), again consistent with the proposed chemistry on the heterogeneous catalyst surface.[11]

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(2) For reviews on the mechanism of propylene ammoxidation see: Keulks, G. W.; Krenzke, L. D.; Notermann, T. M. *Adv. Catal.* **1978**, *27*, 183–225. Haber, J.; Bielanski, A. *Catal. Rev. Sci. Eng.* **1979**, *19*, 1–41. Gates, B. C.; Katzer, J. R.; Schuitt, G. C. A. "Chemistry of Catalytic Processes"; McGraw-Hill, New York, 1979; pp 325–389.

(3) Martir, W.; Lunsford, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 3728–3732.

(4) Burrington, J. D.; Kartisek, C. T.; Grasselli, R. K. *J. Catal.* **1983**, *81*, 489–498; **1984**, *87*, 363–380.

(5) However, oxidation of radicals with C–O bond formation to a ligand oxygen atom is known: Kochi, J. K. *J. Org. Chem.* **1965**, *30*, 1862–1872. Gaudemer, F.; Gaudemer, A. *Tetrahedron Lett.* **1980**, *21*, 1445–1447. Rate constants for oxidation of alkyl radicals by permanganate are close to the diffusion-controlled limit: Streenken, S.; Neta, P. *J. Am. Chem. Soc.* **1982**, *104*, 1244–1248.

(6) An analogy can be made between eq 3 and the rearrangement of allylic and propargylic alcohols promoted by vanadium and tungsten oxo complexes: Hosogai, T.; Fujita, Y.; Ninagawa, Y.; Nishida, T. *Chem. Lett.* **1982**, 357–360 and references therein. See also: Kane, B. J. U.S. Patent 4254291, 1981.

(7) Nugent, W. A. *Inorg. Chem.* **1983**, *22*, 965–969. Nugent, W. A.; Harlow, R. L. *Ibid.* **1980**, *19*, 777–779.

(8) In fact, methylbenzenes, under ammoxidation conditions, are converted to the corresponding benzonitriles in high yield: Sheldon, R. A.; Kochi, J. K. "Metal-Catalyzed Oxidations of Organic Compounds"; Academic Press: New York, 1981; pp 324–325.

(9) Yields of CO_2 from benzoyl peroxide in reactions containing the imido complexes were 84–86% of those in blanks containing no metal by internal standard GLC.

(10) Perkins, M. J. In "Free Radicals"; J. K. Kochi, Ed.; Wiley-Interscience: New York, 1973; Vol. II, pp 231–271.

(11) The observation that yields of **3** have never exceeded 50% based on metal suggests the possibility that eq 7 is a bimolecular process requiring a second equivalent of oxidant.

The tungsten imido complex **5** was employed for model studies on eq 3. Alcoholysis of **5** (eq 8) is known.[7] Heating a 1:1 mixture

$$\underset{\mathbf{5}}{(t\text{-BuNH})_2W(N\text{-}t\text{-Bu})_2} + 2ROH \rightarrow (RO)_2W(N\text{-}t\text{-Bu})_2 + 2\text{-}t\text{-BuNH}_2 \quad (8)$$

of **5** with linalool (toluene, reflux) afforded, after hydrolysis, the rearranged (geranyl and neryl) amines in 90% yield (Table II). Similar results were obtained with other allylic alcohols. It is noteworthy that allyl alcohol-1,1-d_2 afforded a mixture of 22% 1,1- and 78% 3,3-dideuterated allyl-*tert*-butylamines.[12] This observation, along with the results for the isomeric octenols (Table II), suggests that the reaction does not proceed exclusively by a concerted electrocyclic rearrangement of the type implied by eq 3. A competing pathway, perhaps involving an allyl/metalate ion pair, must additionally be involved.

In conclusion, homogeneous analogues of the two C–N bond-forming processes proposed by Grasselli in the ammoxidation of propylene have been observed by us under mild conditions. While these observations constitute neither a necessary nor a sufficient condition for the mechanism of the heterogeneous process to be correct, they lend support to the Grasselli proposals while also opening the way to detailed mechanistic studies of such elemental steps.

Registry No. **2a**, 71851-94-0; **2b**, 71851-95-1; **3**, 6852-58-0; $PhCH_2\cdot$, 2154-56-5; $CH_2{=}CHCH_3$, 115-07-1; PhC(O)OOC(O)Ph, 94-36-0; $(Me_3SiO)_2CrO(N\text{-}t\text{-Bu})$, 83619-58-3.

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Received January 18, 1985

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[12] Scrambling of the isotopic label was also observed during heterogeneous ammoxidation of allyl alcohol-1,1-d_2. Burrington, J. D.; Kartisek, C. T.; Grasselli, R. K. *J. Catal.* **1980**, *63*, 235–254.

[13] Contribution No. 3615.

Articles

Contribution from the Department of Chemistry,
McMaster University, Hamilton, Ontario L8S 4M1, Canada

Chemistry of the Pentacyano(4-nitroimidazolato)ferrate(II) Ion: Unusual Oxidation States of Iron

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Received October 26, 1984

Complexes involving 4-nitroimidazole as a ligand have been little studied. They are of potential interest because of the rather facile reduction of this compound to a radical anion, which raises the possibility of studying metal-complexed radicals or complexes of metals in unusually low oxidation states. An Fe(II) complex containing this ligand associated with the pentacyanoferrate moiety has been synthesized, and its spectroscopic properties are reported. They demonstrate that the 4-nitroimidazolato ion is a strong field ligand. The kinetics of ligand-exchange reactions of this compound have been studied. The rates of association and of dissociation are comparable to those reported for similar pentacyanoferrate(II) complexes. The Fe(II) complex can be oxidized to a thermodynamically less stable Fe(III) compound. More interestingly it can be reduced by sodium dithionite. Stopped-flow spectrophotometry shows that there are two reduction steps, both involving the SO_2^- radical. Both steps are pH dependent and involve simultaneous one-electron reduction and protonation of the complex. ESR spectroscopy establishes that the first reduction product is a pentacoordinate Fe(I) complex. Protonation has occurred on the imidazole ring. Proton NMR of the final product shows a resonance around 20 ppm to high field of Me_4Si, strongly suggesting that the second reduction step is accompanied by protonation on the metal to give a hydridoiron(II) compound. The analogy with the catalytically active isoelectronic pentacyanocobaltate(II) and hydridopentacyanocobaltate(III) ions is noted.

Introduction

Some years ago it was reported that 4-nitroimidazole forms a thermodynamically very stable and kinetically inert complex with metmyoglobin.[1] Of the wide variety of complexes of metmyoglobin known, this complex is second only to that formed with the cyanide ion in terms of the magnitude of the formation constant (8800 M^{-1}) and its slow rate of dissociation ($k = 0.04$ s^{-1}). pH measurements indicated that the complex contained the 4-nitroimidazolato ion rather than the neutral 4-nitroimidazole molecule. These results suggest that the 4-nitroimidazolato ion might form stable complexes with a variety of transition-metal ions.

4-Nitroimidazole and its derivatives show a number of properties that suggest that these metal complexes may be of interest. They have pharmaceutical applications as radiosensitizers and as drugs.[2,3] In the presence of radiation, 4-nitroimidazole is reduced to radical anions, the structures of which have been studied as a function of pH by ESR.[4] It has been suggested that these radical anions are responsible for the radiosensitizer properties. Kinetic studies of the reduction of the myoglobin derivative by dithionite indicated that the electron was transmitted through the 4-nitroimidazole π system and that a radical ligand existed as a transient intermediate. It occurred to us that if the radical ligand were associated with a metal ion less easily reduced than Fe(III), more stable radical complexes might result. We have been interested in such complexes for some years.[5,6] Alternatively the good π-accepting properties of the 4-nitoimidazole ligand might serve to stabilize unusually low oxidation states of metal ions. The question also arises as to how the oxidation/reduction properties of the imidazole ring are linked to the acid/base properties. The potential importance of such linkage in imidazole chemistry to processes such as oxidative phosphorylation has been discussed

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[1] Eaton, D. R.; Wilkins, R. G. *J. Biol. Chem.* **1978**, *253*, 908.

[2] Wardman, P. *Int. J. Radiat. Biol.* **1975**, *28*, 585.

[3] Ayscough, P. B.; Elliot, A. J., Salmon, G. A. *Int. J. Radiat. Biol.* **1975**, *27*, 603.

[4] Whillans, D. W.; Adams, G. E.; Neta, P. *Radiation Res.* **1975**, *62*, 407.

[5] Eaton, D. R. *Inorg. Chem.* **1964**, *3*, 1268.

[6] (a) Cazianis, C. T.; Eaton, D. R. *Can. J. Chem.* **1974**, *52*, 2454. (b) Eaton, D. R.; Plancherel, D. *Can. J. Chem.* **1981**, *59*, 156.

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