

Synthesis and structure of a novel binuclear rhenium(I) complex containing an unusual bridging ligand derived from coordinated acetonitrile. Unusual reactivity of $[\text{Re}(\text{CO})_3(\text{bpy})(\text{MeCN})]^+$

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$[\text{Re}(\text{CO})_3(\text{bpy})(\text{MeCN})]^+$ forms a novel binuclear rhenium(I) complex containing a $\text{N}=\text{CCH}=\text{C}(\text{CH}_3)\text{NH}$ bridge derived from the reaction of the coordinated acetonitrile with NaH ; the crystal structure of which has been determined.

There has always been considerable interest in transition metal nitriles which are extensively used as starting materials for a large variety of coordination and organometallic complexes, as well as in the activation of organonitriles in organic transformation reactions, which result from changes in the electrophilicity or nucleophilicity of the nitrile upon coordination to the metal center.^{1,2} The coordination chemistry of coordinated nitriles at rhenium(I) centers has recently been reviewed,^{1f,2} in which the coordinated nitrile carbon has been observed to be prone to attack by electrophiles such as H^+ . Although there have been reports on the nucleophilic attack on nitriles coordinated to electron-deficient metal centers such as those of Co^{III} ,³ to the best of our knowledge, there has been no report on reactions involving nucleophilic attack on the nitriles coordinated to rhenium(I) metal centers, which are normally accepted as being electron rich. Complexes such as $[\text{ReCl}(\text{NCR})(\text{dppe})_2]$ have been reported to undergo protonation at the nitrile carbon, due to the strong π electron releasing ability of the Re^{I} center to the NC π^* orbitals of the coordinated nitrile,^{1f,2} to yield azavinylidene derivatives. Herein we report the unusual reactivity of $[\text{Re}(\text{CO})_3(\text{bpy})(\text{MeCN})]^+$ and the first example of a nucleophilic attack at the nitrile coordinated to the rhenium(I) center. The crystal structure of the novel binuclear rhenium(I) product, $[\{\text{Re}(\text{CO})_3(\text{bpy})\}_2\{\text{NHC}(\text{CH}_3)\text{CHCN}\}]^+$ **1** has also been determined.

Reaction of $[\text{Re}(\text{CO})_3(\text{bpy})(\text{MeCN})]\text{OTf}$ (0.5 mmol) with NaH (0.3 mmol) in thf (20 ml) at room temp. for 2 min under nitrogen afforded a reddish brown solution, which was then purified by column chromatography on silica gel using dichloromethane–acetone (1:1 v/v) as eluent to yield $[\{\text{Re}(\text{CO})_3(\text{bpy})\}_2\{\text{NHC}(\text{Me})\text{CHCN}\}]^+$ as dark red crystals; the identity of which has been confirmed by characterization with ^1H NMR, ^{13}C NMR, IR, FABMS, elemental analyses,[†] and X-ray crystallography.[‡]

The perspective drawing of the complex cation of **1** is depicted in Fig. 1. The structure of the complex consists of two rhenium diimine moieties bridged by an enamino–nitrile ligand. The coordination geometry at each Re atom is distorted octahedral with the three carbonyl ligands arranged in a *fac* fashion.⁴ Bond distances worthy of special comment are $\text{N}(4)–\text{C}(16)$ [1.29(1) Å], which is indicative of a C–N bond

intermediate between those of single and double bond character, $\text{C}(14)–\text{C}(15)$ [1.40(1) Å] and $\text{C}(15)–\text{C}(16)$ [1.41(2) Å] which are intermediate between those expected for single and double bonds and are closer to that expected for alkenes. Although the bond distance $\text{N}(3)–\text{C}(14)$ [1.13(1) Å] is quite short, the IR stretching frequency for the $\text{C}=\text{N}$ bond is 2194 cm^{-1} , which is at lower frequency than that found in $[\text{Re}(\text{CO})_3(\text{bpy})(\text{MeCN})]^+$ (2315 cm^{-1}),[§] and may be suggestive of a bond weaker than that for a true triple bond character. These data strongly suggest that the π bonding or electron is extensively delocalized over the NCCCN moiety of the bridging ligand (Scheme 1). Such delocalization has also been observed in other systems.⁵ The enamino–nitrile ligand containing $\text{N}(3)$, $\text{C}(14)$, $\text{C}(15)$, $\text{C}(16)$ and $\text{N}(4)$ shows a coplanar arrangement with a mean deviation of 0.0114 Å from the least-squares plane, which is in accordance with the π bonding being delocalized over the NCCCN moiety.

The room temp. ^1H NMR spectrum shows two sets of chemical shifts for each resonance signal of CH_3 , NH and CH groups. This has been attributed to the presence of two conformers existing in equilibrium in solution. The two

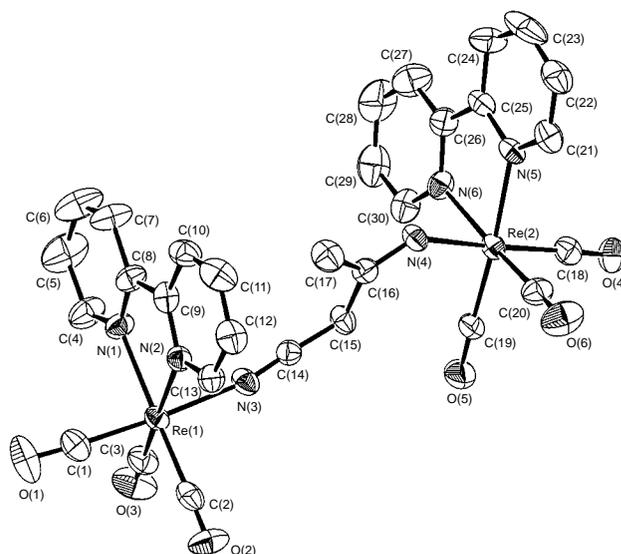
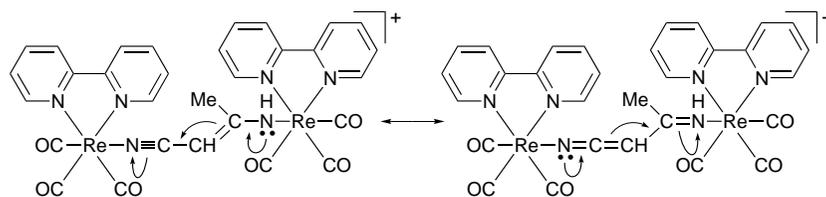
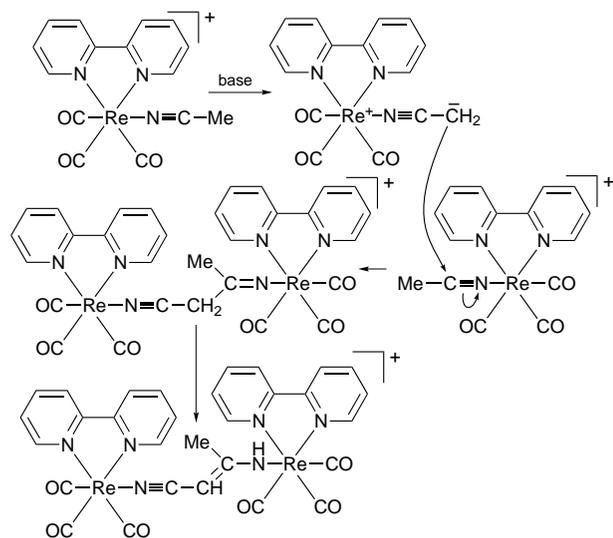


Fig. 1 Perspective drawing of the complex cation of **1** with atomic numbering scheme. Thermal ellipsoids are shown at the 40% probability levels.



Scheme 1



Scheme 2

conformers or rotamers are the *cis*- and *trans*-isomers owing to the restricted rotation about the C=C bond in the N=CC=C system. The two isomers are in equilibrium, resulting from the mesomerism, and the relative populations of the isomers change with different solvent polarities, which are common in organic compounds with the O=CC=CN moiety.⁶ The relative populations of the *cis*- and *trans*-isomers are *ca.* 7 : 1 in acetonitrile and *ca.* 5 : 1 in acetone. The ¹³C NMR spectrum also shows two distinct resonances for CH₃ and CH groups which are in accord with results obtained from ¹H NMR spectroscopy; the identities of the CH₃ and CH signals have also been confirmed by DEPT-135 NMR spectroscopy.

A mechanism involving the initial deprotonation of the α -methylene proton in the coordinated acetonitrile in the presence of a strong base to give the carbanion [Re(CO)₃(bpy)(N≡CCH₂)], followed by its attack on the electrophilic nitrile carbon of a second molecule of [Re(CO)₃(bpy)(MeCN)]⁺, is proposed. The imine group in the bridging ligand finally tautomerizes to the enamine, despite the fact that imine is commonly more stable than enamine (Scheme 2). It is likely that the presence of delocalization of electron over the bridging ligand in this enamino–nitrile form favors the tautomerism. The deprotonation step has also been proposed to occur in other electron-deficient transition metal nitrile complexes.³ It is likely that the Re^I center in [Re(CO)₃(bpy)(MeCN)]⁺ which carries a positive charge and contains strong π -accepting CO groups, unlike the neutral [ReCl(RCN)(dppe)₂], is fairly electron deficient, and is thus capable of activating the coordinated acetonitrile towards deprotonation. The electrophilic nature of Re^I has been reflected by the higher $\nu(\text{C}\equiv\text{N})$ stretching frequencies observed in [Re(CO)₃(bpy)(MeCN)]⁺ than in free acetonitrile.⁷ Similar frequency shifts have been reported for the cobalt(III) complexes which have been proposed to undergo base hydrolysis *via* an initial deprotonation step.³ Preliminary studies show that [{Re(CO)₃(bpy)}₂{NHC(Me)CHCN}]⁺ is strongly luminescent, typical of triplet MLCT emission in related rhenium(I) diimine systems.^{5,8}

The detailed photophysical and reactivity studies of this complex, as well as the preparation of related complexes containing different bridging ligands by employing coordinated nitriles other than acetonitrile, are in progress.

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Footnotes and References

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† Characterization of **1**. ¹H NMR [300 MHz, (CD₃)₂CO, 298 K, relative to TMS]: δ 1.20, 1.54 (s, 3 H, CH₃), 3.10, 3.82 (s, 1 H, CH), 5.12, 5.68 (s, 1 H, NH), 7.78 (t, 2 H, bpy), 7.90 (t, 2 H, bpy), 8.34 (t, 2 H, bpy), 8.42 (t, 2 H, bpy), 8.74 (d, 2 H, bpy), 8.80 (d, 2 H, bpy), 9.00 (d, 2 H, bpy), 9.20 (d, 2 H, bpy). ¹³C{¹H} NMR [67.9 MHz, (CD₃)₂CO, 298 K, relative to TMS]: δ 24 (CH₃), 52 (CH), 126 (bpy), 129 (bpy), 137 (C≡N), 142 (bpy), 155 (bpy), 157 (NHCMeCHCN), 177 (C=O), 199 (C=O). IR (Nujol, cm⁻¹): $\nu(\text{NH})$ 3302; $\nu(\text{C}\equiv\text{N})$ 2172; $\nu(\text{C}=\text{O})$ 2027, 2014, 1936, 1903. Positive ESIMS: ion clusters at m/z 933 [M]⁺, 905 [M - CO]⁺, 509 [M - [Re(bpy)(CO)₃]]⁺. UV-VIS [λ/nm ($\epsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)] (MeCN) 246 (41 460), 314 (42 360), 338 (27 280), 450 (1280). Found: C, 34.25; H, 1.88; N, 7.79. Calc. for 1-H₂O: C, 34.82; H, 2.15; N, 7.86%.

‡ Crystal data for **1**: {[Re₂O₆N₆C₃₀H₂₁]⁺CF₃SO₃⁻}; $M = 1083.01$, monoclinic, space group $P2_1/c$ (no. 14), $a = 10.632(2)$, $b = 16.607(2)$, $c = 20.611(3)$ Å, $\beta = 103.83(2)^\circ$, $U = 3533.7(10)$ Å³, $Z = 4$, $D_c = 2.036$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 69.83$ cm⁻¹, $F(000) = 2056$, $T = 301$ K. Convergence for 448 variable parameters by least squares refinement on F with $w = 4 F_o^2/\sigma^2(F_o^2)$ where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.020F_o^2)^2]$ for 3915 reflections with $I > 3\sigma(I)$ was reached at $R = 0.034$ and $wR = 0.043$ with a goodness-of-fit of 2.18. CCDC 182/680.

§ Assignment of $\nu(\text{C}\equiv\text{N})$ for [Re(CO)₃(bpy)(MeCN)]⁺ is confirmed by comparison with [Re(CO)₃(bpy)(CD₃CN)]⁺.

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