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Two-Electron Reductive Coupling of Acetonitrile To Form a (*μ*-Butane-2,3-diimino(2−)-*N*:*N*′)ditungsten Complex

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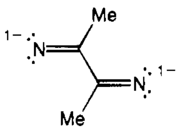
Introduction

The formation of carbon−carbon bonds and the stabilization of highly reactive, otherwise unstable ligands by metal centers are central themes in organometallic chemistry.[1,2] The reductive coupling of organonitrile ligands, a reaction with considerable intrinsic and practical appeal, embodies both themes. Here, we describe the synthesis and X-ray structure of [$\{HB(Me_2pz)_3\}W(CO)_2]_2\{\mu$-NC(Me)C(Me)N-*N*:*N*′} [**1**, $HB(Me_2pz)_3^-$ = hydrotris(3,5-dimethylpyrazol-1-yl)borate anion]. The complex results from the two-electron reductive coupling of acetonitrile and the formation of a carbon-carbon bond between the nitrile carbon atoms. It features a bridging *anti*-butane-2,3-diimino-(2−)-*N*:*N*′ ligand, L, which to our knowledge is the first of its kind to be structurally characterized. The neutral parent *anti*-butane-2,3-diimine appears to be highly unstable and has never been isolated.



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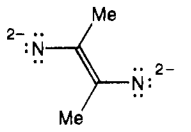

L′

The four-electron reductive coupling of acetonitrile has been reported and a number of complexes containing the (*E*)-butene-2,3-diimido(4−)-*N*:*N*′ ligand, L′, have been isolated and structurally characterized.[3−8] Reaction of MCl_4 (M = Nb,[3] Ta[3,4]) and zinc in acetonitrile produced green complexes, presumably $[MCl_3(MeCN)_2]_2(\mu$-L′), which were converted to $[N(PPh_3)_2]_2\{[MCl_4(MeCN)]_2(\mu$-L′)} upon reaction with $[N(PPh_3)_2]Cl$. The crystal structure of the niobium salt, reported by McCarley and co-workers[3] in 1975, confirmed the dinuclear structure and the presence of the *μ*-L′ ligand. Subsequently, Cotton and Hall[5] recrystallized "$[TaCl_3(MeCN)_2]_2$"[6] from tetrahydrofuran (THF) and structurally characterized the product, $[TaCl_3(THF)_2]_2(\mu$-L′). These workers also reported an improved synthesis for $[TaCl_3(MeCN)_2]_2(\mu$-L′).[7] More recently, Gambarotta and coworkers[8] characterized $[TiCl_2(TMEDA)]_2(\mu$-L′) (TMEDA = *N,N,N′,N′*- tetramethylethylenediamine), which was formed upon reaction of $TiCl_2$(TMEDA) and acetonitrile. Structural parameters were consistent with bridging enediimido ligands in these formally d^0 complexes. Complexes containing the diimino ligand L have been prepared by de Bier and Teuben,[9] who isolated $[Cp_2TiR]_2(\mu$-L) (Cp = η^5-$C_5H_5^-$; R = aryl, Cl) complexes upon reaction of Cp_2TiR with MeCN. These complexes have not been structurally characterized.

Table 1. Crystallographic Data for **1**

formula	$C_{19}H_{25}BN_7O_2W$	*c*, Å	24.407(14)
fw	578.11	*β* (deg)	115.24(5)
cryst dimens, mm³	0.25 × 0.25 × 0.25	*V*, Å³	4956(5)
cryst color	blue	Z	8
cryst syst	monoclinic	*D*(calc), g cm⁻³	1.55
space group	*C*2/*c*	*μ*(Mo Kα), mm⁻¹	4.79
a, Å	21.662(15)	R[a]	0.064
b, Å	10.3633(17)	R_w[a]	0.077

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Experimental Section

Preparation of [$\{HB(Me_2pz)_3\}W(CO)_2]_2\{\mu$-NC(Me)C(Me)N-*N*:*N*′}, 1. A mixture of $\{HB(Me_2pz)_3\}W(CO)_3Br$[10] (0.5 g, 0.78 mmol) and NaS^iPr (0.08 g, 0.82 mmol) in dry (CaH_2), deoxygenated acetonitrile (25 mL) was refluxed under nitrogen for 2 h. After cooling, the mixture was filtered in air and the filtrate was treated with petroleum ether (40−60 °C bp) and cooled at 4 °C for 2 days. Diffraction quality crystals of **1** were isolated by filtration. Yield: 67 mg, 15%. IR (KBr): 2920 w, 2550 w, *ν*(CO) 1915 s and 1810 s, 1620 w, br, 1580 w, br, 1535 s, 1445 s, 1410 s, 1360 s, 1200s, 1180 s, 1060 s, 980 w, 905 w, 855 w, 810 w, 780 w, 730 w, 690 w, 640 w cm⁻¹.

X-ray Crystal Structure of 1. Crystallographic data are summarized in Table 1. The unit cell parameters were obtained from least-squares fit of 64 reflections in the range $30° \le 2\theta \le 40°$. Intensity data were collected in the $\theta-2\theta$ scan mode on a Rigaku AFC6/S diffractometer using Mo Kα radiation at 23 °C. Only data with $I > 2.5\sigma(I)$ were used in the structure solution and refinement.[11] The data were corrected for Lorentz and polarization effects. Absorption corrections were based on *ψ*-scans corrected for mean crystal size. The minimum and maximum transmission factors were 0.345 and 0.483, respectively. The structure was solved using Patterson and Fourier methods and refined by a full-matrix least-squares procedure, using 1757 data, to a conventional *R* value of 0.064 (R_w = 0.077).[12] The highest peak in the final Fourier map was 1.70 e Å⁻³. The final atomic coordinates are given in Table 2. An ORTEP[13] view of the molecule and selected bond distances and angles are given in Figure 1.

Results and Discussion

Reaction of $\{HB(Me_2pz)_3\}W(CO)_3Br$ with NaS^iPr in refluxing acetonitrile resulted in the formation of **1** as the major carbonyl containing product. The initial product of the reaction exhibited two *ν*(CO) bands at 1865 and 1735 cm⁻¹. With time it was transformed into **1**, which exhibited two *ν*(CO) bands at 1925 and 1815 cm⁻¹. One interpretation of these observations

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Table 2. Positional Parameters and Their Estimated Standard Deviations for **1**

atom	*x/a*	*y/b*	*z/c*	*B*,[a] Å^2
W	0.94762(6)	0.22082(10)	0.10275(5)	2.47(4)
O(1)	0.9014(9)	−0.0353(17)	0.0290(8)	4.0(11)
O(2)	1.0774(9)	0.0932(18)	0.1040(8)	4.6(12)
N(1)	0.9630(10)	0.1361(19)	0.1755(9)	2.7(11)
N(11)	0.9291(10)	0.3429(20)	0.0226(9)	2.9(12)
N(12)	0.9021(10)	0.4694(19)	0.0217(9)	3.2(13)
N(21)	0.8447(9)	0.2890(21)	0.0883(8)	3.1(11)
N(22)	0.8355(10)	0.4321(19)	0.0847(9)	2.9(12)
N(31)	0.9873(10)	0.4114(19)	0.1524(9)	3.0(12)
N(32)	0.9534(10)	0.5203(19)	0.1318(9)	3.0(12)
C(1)	0.9167(14)	0.0640(30)	0.0572(12)	3.8(16)
C(2)	1.0317(12)	0.1544(24)	0.1025(11)	2.6(14)
C(3)	0.9681(11)	0.0855(22)	0.2251(10)	2.2(13)
C(4)	0.9100(13)	0.0276(24)	0.2343(11)	3.2(15)
C(13)	0.8932(12)	0.5221(24)	−0.0313(11)	2.6(14)
C(14)	0.9127(13)	0.4392(25)	−0.0615(12)	3.4(15)
C(15)	0.9343(12)	0.3282(23)	−0.0283(11)	2.8(14)
C(16)	0.8642(14)	0.6520(30)	−0.0487(13)	4.5(18)
C(17)	0.9608(13)	0.2100(30)	−0.0423(11)	3.7(15)
C(23)	0.7710(14)	0.4520(30)	0.0796(12)	3.6(16)
C(24)	0.7438(13)	0.3350(30)	0.0808(12)	3.8(16
C(25)	0.7894(11)	0.2414(22)	0.0844(10)	2.6(13)
C(26)	0.7484(15)	0.5880(30)	0.0771(13)	4.9(18)
C(27)	0.7818(13)	0.1030(30)	0.0848(12)	3.6(16)
C(33)	0.9893(12)	0.6190(23)	0.1660(11)	2.7(14)
C(34)	1.0452(12)	0.5745(23)	0.2075(11)	2.4(14)
C(35)	1.0454(13)	0.4379(25)	0.1994(12)	3.2(16)
C(36)	0.9632(13)	0.7565(24)	0.1557(11)	3.5(15)
C(37)	1.1022(14)	0.3450(30)	0.2364(13)	4.4(18)
B	0.8901(15)	0.5180(30)	0.0774(14)	2.8(17)

[a] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

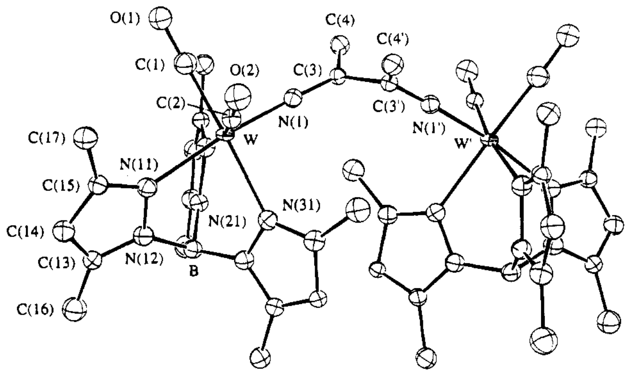

Figure 1. Molecular structure of **1**. The numbering of the pyrazole rings containing N(21) and N(31) parallels that shown for the ring containing N(11). Bond distances (Å) and angles (deg) include the following: W−C(1) 1.92(3), W−C(2) 1.949(23), W−N(1) 1.879(19), W−N(11) 2.219(20), W−N(21) 2.220(18), W−N(31) 2.284(20), C(1)−O(1) 1.20(3), C(2)−O(2) 1.16(3), N(1)−C(3) 1.28(3), C(3)−C(3′) 1.40(4), C(3)−C(4) 1.50(3); C(1)−W−C(2) 78.2(11), W−N(1)−C(3) 173.9(19), N(1)−C(3)−C(4) 124.5(20), N(1)−C(3)−C(3′) 118.5(21), C(3′)−C(3)−C(4) 116.9(21).

is initial reduction of {HB(Me$_2$pz)$_3$}W(CO)$_3$Br by NaS^{i}Pr to form {HB(Me$_2$pz)$_3$}W^{I}(CO)$_2$(MeCN), NaBr and ^{i}PrSS^{i}Pr. The reduced acetonitrile complex, which may possess iminyl radical character, viz. {HB(Me$_2$pz)$_3$}W^{II}(CO)$_2$(Me$\dot{C}$N), may then undergo a coupling reaction to form **1**.[14] The net reaction may be written as eq 1.

$$2\{HB(Me_2pz)_3\}W(CO)_3Br + 2NaS^iPr + 2MeCN \rightarrow \mathbf{1} + 2NaBr + {}^iPrSS^iPr + 2CO \quad (1)$$

Complex **1** was isolated in low yield as diffraction quality crystals. The synthesis of **1** contrasts with the generation of {HB(Me$_2$pz)$_3$}W(CO)$_2$(SR) complexes upon reaction of {HB(Me$_2$pz)$_3$}W(CO)$_2$I with NaSR or HSR in CH$_2$Cl$_2$ or THF at room temperature.[15]

An X-ray diffraction study of **1** revealed a dimeric complex composed of distorted octahedral *fac*-{HB(Me$_2$pz)$_3$}W(CO)$_2$ fragments bridged by an *anti*-butane-2,3-diimino(2−)-*N*:*N′* ligand (Figure 1). The halves of the molecule are related by a crystallographically imposed 2-fold axis through the C(3)−C(3′) bond. The structural parameters of the bridging butanediimino ligand may be compared and contrasted with those of related L′ complexes of Nb,[3] Ta,[5] and Ti,[8] and imido, amido and azavinylidene derivatives of *fac*-{HB(Me$_2$pz)$_3$}W(CO)$_2$.[16−18] Table 3 compares the bridge ligand parameters of known L′ complexes with those of the title complex. Importantly, as we shall now discuss, the structural parameters of the bridge ligand of **1** are significantly different from those consistently found for complexes of L′.

For **1**, the C(3)−C(3′) bond distance of 1.40(4) Å is longer than those of L′ complexes (average 1.35 Å) but slightly shorter than might be expected for an N═C−C═N single bond (*ca.* 1.45 Å).[19] The C(3)−N(1) distance of 1.28(3) Å is typical of a C═N double bond (cf. C−N = 1.47 Å, C═N = 1.27 Å[19,20]). It is consistent with values reported for mononuclear complexes of linear imino complexes (average C−N for N═CR$_2$ = 1.27 Å) and Schiff base complexes containing RN═CR$_2$ moieties (average 1.29 Å).[21] The C(3)−N(1) bond is considerably shorter than imido complexes in general (average 1.42 Å), and the enediimido complexes in particular (Table 3, C−N > 1.38 Å); the latter complexes contain N−C single bonds.[3−5] The C(3′) atoms are trigonal (maximum deviation from plane containing N(1), C(3), C(4), and C(3′) = 0.007 Å, angles 116.9−124.5°, average 120°) consistent with sp^2 hybridization of these atoms. Significantly, however, the bridging ligand is not planar and the dihedral angle between the two NC(Me)−C planes is 54.4°. This is clearly indicative of the absence of any significant π-bonding interaction between the C(3) and C(3′) atoms. In contrast, the atoms of the L′ ligands in the Nb, Ta and Ti complexes are strictly planar. The C(3)−N(1)−W angle of 173.9(2)° is consistent with sp hybridization of the N(1) atoms. There is a significant difference in the M−N distances in the two classes of compound listed in Table 3. Whereas short M−N distances (<1.75 Å) are characteristic of the enediimido complexes,[3−5] and imido complexes in general,[22,23] a longer W−N(1) distance (1.88(2) Å) is observed for **1**. The W−N(1) distance in **1** falls roughly between the W−N distances in structurally characterized amido and imido derivatives of {HB(Me$_2$pz)$_3$}W(CO)$_2$.[17] Each tungsten center in **1** has an azavinylidene unit similar to those found in {HB(Me$_2$-

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(14) In the synthesis of **1**, the compound removed by the filtration step has been spectroscopically and crystallographically characterised as L^{Br}W(CO)Br(η^2-MeCN), where L^{Br} = hydrotris(4-bromo-3,5-dimethylpyrazol-1-yl)borate. This observation provides indirect support for the involvement of monomeric acetonitrile complexes in the formation of **1**. Thomas, S; Young, C. G. Unpublished results.

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Table 3. Structural Comparison of W(μ-L)W and M(μ-L′)M Fragments

complex	M−N, Å	N−C, Å	C−C, Å	M−N−C, deg	C_4N_2 core
1 (this work)	1.88(2)	1.28(3)	1.40(4)	173.9(2)	nonplanar
$\{[NbCl_4(MeCN)]_2(\mu\text{-L}')\}^{2-}$ [3]	1.75(1)	1.38(1)	1.35(1)	178.1(6)	planar
$[TaCl_3(THF)_2]_2(\mu\text{-L}')$[5]	1.747(7)	1.40(1)	1.35(2)	178.7(9)	planar
$[TiCl_2(TMEDA)]_2(\mu\text{-L}')$[8]	1.699(4)	1.384(5)	1.34(1)	175.2(4)	planar

$pz)_3\}W(CO)_2(N{=}CRR')$ compounds (R = H, R′ = ^{n}Pr or Ph); for **1**, R = Me and R′ = $C(Me)NW(CO)_2\{HB(Me_2pz)_3\}$. There is no significant lengthening of the W−N(11) bond *trans* to the W−N(1) bond in **1**; in contrast, the Ta−O bond *trans* to the Ta−N bond in $[TaCl_3(THF)_2]_2(\mu\text{-L}')$ is 0.205 Å longer than the other Ta−O bond in this molecule. This is consistent with a reduction in the bond order and *trans* influence of the W−N(1) bonds of **1** compared to the corresponding M−N bonds in the enediimido complexes. The C(3)−C(4) distance of 1.50(3) is typical of a single bond between sp^2 and sp^3 carbon atoms.[19] The orientation of the $\{HB(Me_2pz)_3\}W(CO)_2$ fragments with respect to the bridging ligand L is also in accord with expectations based on orbital considerations.[17] π-Orbital interactions between the carbonyl ligands and tungsten and between N(1) and tungsten occur when the p_y orbital of N interacts with the tungsten d_{yz} orbital [with z along W−N(1) and x bisecting the C(1)−W−C(2) angle]. With the W−N(1) and N(1)−C(3) π systems necessarily orthogonal, the C(Me)-R′ fragment is expected to be orthogonal to the pseudomirror plane of the $\{HB(Me_2pz)_3\}W(CO)_2$ fragment, as observed. In short, the distances and angles observed in the bridging ligand present in **1** are only consistent with a formal butane-2,3-diimino(2−) electronic description for the bridging ligand.

The ligands L and L′ differ by two electrons and hence are not related as resonance structures. Once a metal is attached to each terminal nitrogen, the metal oxidation state can be formally altered to accommodate either ligand formulation, but the implications for molecular properties are substantial. The structural results above confirm the presence of L in **1**. The alternative description of **1** as an L′ complex would require two W(III) centers in the complex. Unlike the complexes of L′, where d^0 metal configurations accompany the tetraanion ligand formulation, the ancillary π-acid carbonyl ligands in **1** favor, for back-bonding purposes, a low tungsten oxidation state, viz. W(II), is preferred.

Tetrakis(dimethylamino)ethene and the corresponding dication display interesting structural parallels with the enediimido and diimino ligands in the complexes discussed in this paper. Thus, the N−C bonds shorten and the C−C bond lengthens upon two-electron oxidation of $(Me_2N)_2C{=}C(NMe_2)_2$. In the chloride salt, the dication possess average N−C and C−C distances of 1.31 and 1.55 Å, respectively. The lengthening of both relative to the corresponding bonds in **1** is no doubt due to delocalization of the positive charge over all four nitrogen atoms, a feature not possible in the case of L.[24]

The niobium and tantalum complexes of L′ were formed in reactions involving M(IV), a reducing agent and acetonitrile, or by direct reaction of the Ta(III) complex $Ta_2Cl_6(SC_4H_8)_3$ with acetonitrile;[3−7] a possible role for d^2 M(III) is implicated. In the chemistry reported by Gambarotta *et al.*,[8] a d^2 Ti(II) complex undergoes reaction with acetonitrile to produce the observed product. As the products of these reactions are best described as d^0 enediimido species, it is evident that the full reducing power of two metal centers is exploited in the four-electron reductive coupling of acetonitrile. The redox half-reactions are as follows (the numbers in parentheses specify formal metal oxidation states):

$$2M(n) \rightarrow 2M(n+2) + 4e^-$$

$$2MeCN + 4e^- \rightarrow L'$$

In the synthesis of **1** the generation of a diimino complex is a likely consequence of the use of a one-electron reductant (S^iPr^-) and the fortuitous matching of reductant and W(II)/W(I) redox potentials. Coordination of acetonitrile to W(I) sets the scene for the two-electron coupling of acetonitrile, with the eventual formation of **1**, as the metal centers are reoxidized to W(II). In summary:

$$2W(II) + 2S^iPr^- \rightarrow 2W(I) + {}^iPrSS^iPr$$

$$2W(I) \rightarrow 2W(II) + 2e^-$$

$$2MeCN + 2e^- \rightarrow L$$

The low-valent state of the metal center favors the formation of the diimino complex rather than an enediimido complex, which would in turn be favored in the case of high-valent metal complexes of Nb(V), Ta(V) and Ti(IV). Interestingly, the only other reported complexes of L were formed upon reaction of acetonitrile with the Ti(III) complexes Cp_2TiR, which in the formation of the dimer $[Cp_2TiR]_2(\mu\text{-L})$ are able to provide an electron per Ti for the two-electron reductive coupling of acetonitrile. The selective use of one-electron reductants may permit an expansion of the two-electron reductive coupling reaction reported here and thereby open new applications in organometallic and organic chemistry.

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Supporting Information Available: Full tables of positional and thermal parameters, bond distances, bond angles, and least-squares planes (5 pages). Ordering information is given on any current masthead page.

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