

Inorganica Chimica Acta 337 (2002) 11-31



www.elsevier.com/locate/ica

Mo/W $-N_2$ and $-N_2H_2$ complexes with *trans* nitrile ligands: electronic structure, spectroscopic properties and relevance to nitrogen fixation

Carsten M. Habeck, Nicolai Lehnert, Christian Näther, Felix Tuczek*

Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel, Olshausenstraße 40, D-24098 Kiel, Germany

Received 16 January 2002; accepted 8 April 2002

Dedicated to Professor Dr. Karl Wieghardt on the occasion of his 60th birthday

Abstract

Molybdenum and tungsten dinitrogen complexes with *trans* nitrile groups are of significant interest to synthetic nitrogen fixation as they can be protonated to the corresponding N_2H_2 complexes with retention of the *trans* ligand. This is in contrast to their bis(dinitrogen) counterparts where one N_2 group is exchanged by a ligand X deriving from the acid used for protonation (X = Hal⁻, HSO₄⁻ etc.). Here the first crystal structure of a tungsten(0) dinitrogen nitrile complex having a P_4 ligand set is presented. The electronic and vibrational properties of this and analogous N_2 and N_2H_2 systems with *trans* nitrile ligands are investigated using IR and Raman spectroscopies coupled to DFT calculations. Force constants are evaluated from experimental frequencies and isotope shifts by the QCA–NCA procedure developed earlier [N. Lehnert, F. Tuczek, Inorg. Chem. 38 (1999) 1659]. The resulting electronic structure descriptions are compared with those obtained earlier for the bis(dinitrogen) and *trans* fluoro N_2H_2 complexes, respectively [N. Lehnert, F. Tuczek, Inorg. Chem. 38 (1999) 1671]. Importantly, the N_2 ligand is found to be activated to a higher degree in the *trans* nitrilo as compared with the corresponding bis(dinitrogen) system. On the other hand, the N_2H_2 ligand is less activated in the *trans* nitrilo than in the analogous *trans* fluoro complexes. Further, bonding of the nitrile group becomes labile at the N_2H_2 stage of N_2 reduction. These results are interpreted based on the electronic donor/acceptor properties of the respective *trans* ligands, and the consequences regarding the reactivity of these systems towards further protonation and their potential use for synthetic nitrogen fixation are discussed.

© 2002 Published by Elsevier Science B.V.

Keywords: Nitrogen fixation; Dinitrogen complexes; Hydrazido(2-) complexes; Nitrile complexes

1. Introduction

A synthetic route to nitrogen fixation under ambient conditions is one of the classic goals of bioinorganic, metal-organic and coordination chemistry. This requires a detailed knowledge of the specific conditions for the activation and reduction of dinitrogen. It has been demonstrated that information relevant to this subject can be obtained from the investigation of well-defined model complexes that are able to bind and reduce N₂ [1]. In nature nitrogen fixation is mediated by the enzyme nitrogenase [2] which is composed of two components, the iron- (Fe-) and the molybdenum-iron (MoFe-)

protein. It is believed that N₂ is bound and reduced to NH₃ at the iron-molybdenum cofactor (FeMoco), a unique Fe₇MoS₉ cluster present in the MoFe protein. One possible coordination geometry of N_2 to the FeMoco involves the end-on terminal coordination [3] which also exists in simple mononuclear Mo/W-N₂ complexes of the type $[M(N_2)_2(P_4)]$, where M = W or Mo and P is one phosphorus donor of mono- or bidentate phosphine ligands. Remarkably, these systems can be protonated in a stepwise manner leading to welldefined intermediates [4]. The hypothesis has been put forward that protonation of N2 in nitrogenase proceeds in a similar manner as in these low molecular-weight complexes [5]. In this sense they can be considered as functional models for the end-on terminal reduction and protonation pathway of nitrogenase.

^{*} Corresponding author. Tel.: +49-431-880 2406; fax: +49-431-880 1520

^{0020-1693/02/\$ -} see front matter \odot 2002 Published by Elsevier Science B.V. PII: S 0 0 2 0 - 1 6 9 3 (0 2) 0 0 9 8 8 - X

The bis(dinitrogen) complexes of Mo and W react with mineral acids to give 'diazenido(-)' (NNH⁻), (NNH_2^{2-}) and 'hydrazido(2-)' 'hydrazidium' (NNH_3^{-}) compounds which in the case of bidentate phosphine coligands have been structurally and spectroscopically characterized [4]. After the splitting of the N-N bond, nitrido-, imido- and amido species have been identified [6]. Our research involves the detailed spectroscopic and quantum-chemical characterization of these complex-bound intermediates as well as the study of the proton and electron transfer steps involved in their interconversion in order to further explore the physicochemical conditions under which a catalytic cycle based on such systems could actually work [1a,7].

An ideal metal complex for the homogeneous catalysis of nitrogen fixation should provide a framework for the binding and reduction of N₂ that stays more or less intact during the entire catalytic cycle. From this perspective, one of the serious drawbacks of the mentioned Mo/W bis(dinitrogen) systems is the exchange of one N2 group in the very first protonation step against a ligand X (Hal⁻, HSO₄⁻ etc.). This strongly affects the electronic structure of the metal complex mediating the transformation of N₂ to NH₃. From the viewpoint of catalysis, it also corresponds to a loss of 50% of bound substrate. In the cases reported so far, X is either identical with the conjugated base of the mineral acid employed in the protonation (e.g. HSO_4^{-}), or X is a Lewis base being contained in the conjugated base of that acid (e.g. F^- in BF_4^-). The ligand exchange obviously represents an unwanted kinetic barrier to the metal-centered reduction and protonation of N_2 , and therefore systems are desirable which avoid this process.

In this respect, it is noteworthy that $Mo/W-N_2$ complexes with *trans*-nitrile groups have been shown to be protonable on the N2 ligand without ligand exchange. Studies on their reactivity, [8] their electrochemical [9] and NMR spectroscopic [10] properties have been performed earlier. Electrochemical oxidation potentials have been correlated with trends from N-N and C-N stretching frequencies [9]. In addition, nitriles have been used to attach Mo/W-N2 complexes to electrodes for the electrosynthesis of ammonia [11]. In this study, we compare Mo/W-dinitrogen and -hydrazido(2-) systems with *trans* nitrile ligands to their bis(dinitrogen) and trans fluoro counterparts, respectively, which we have investigated earlier [7]. In particular, spectroscopy coupled to quantum-chemical calculations (DFT) is employed in order to quantitatively describe the bonding and activation of the N_2 and N_2H_2 groups in these systems.

The results of IR and Raman spectroscopic investigations are evaluated with a quantum-chemistry assisted normal coordinate analysis (QCA–NCA) which in conjunction with the DFT calculations allows to obtain detailed insight into the electronic structure of these intermediates. Since the DFT calculations require structural input, a crystal structure determination of the *trans* nitrilo dinitrogen complex $[W(N_2)(NCEt)(dppe)_2]$ has been carried out. This represents the first crystallographic information available for this class of compounds. The consequences of the bonding descriptions of the N₂ and N₂H₂ intermediates with *trans* nitrile ligands with respect to the design of a catalyst for N₂ reduction and protonation are discussed.

2. Experimental

2.1. Synthesis, isotopic substitution and sample preparation

The dinitrogen complexes of tungsten (I, III, V) as well as the protonated species (II, IV) with the dppe (dppe = bis(diphenylphosphino)ethane) ligand were prepared following literature procedures [8,12] with slight variations. The nitrile group was introduced by irradiation of a solution of the bis(dinitrogen) complex with a 100 W tungsten lamp in the presence of an excess of the respective nitrile. For protonation, degassed sulfuric acid (96%) was used. Protonation with HBF₄ was found to lead to decomposition of the nitrile $-N_2$ complexes. All protonated species could be deprotonated to the corresponding dinitrogen complexes with triethylamine. The ¹⁵N isotopomer of $W(^{15}N_2)_2(dppe)_2$, **0b**, was synthesized using ${}^{15}N_2$. The ${}^{15}N$ labeled compounds $W(^{15}N_2)(NCEt)(dppe)_2$, **Ib**, $[W(^{15}N_2H_2)(NCEt)(dppe)_2]$ - $(HSO_4)_2$, IIb, $W(^{15}N_2)(NCPr^n)$ (dppe)₂, IIIb, $[W(^{15}N_2 H_2$)(NCPrⁿ)(dppe)₂](HSO₄)₂, **IVb**, and W(¹⁵N₂)-(NCPh)(dppe)₂, Vb, were prepared from the ¹⁵N substituted complex 0b. Because the compounds are air sensitive, syntheses were performed using the Schlenktechnique. The dinitrogen-nitrile systems I and III exchange nitrile against dinitrogen within weeks in the solid state. In solution, the exchange is much faster. Sample preparation for vibrational spectroscopy was carried out in a glovebox. All liquid reagents and solvents were dried under argon or dinitrogen gas, with the exception of sulfuric acid which was degassed by treatment in an ultrasonic bath.

 $W(N_2)_2(dppe)_2$ (0), obtained as orange solid in 50% yield. *Anal*. Calc. for C₅₂H₄₈N₄P₄W: C, 60.2; H, 4.7; N, 5.4. Found: C, 59.1; H, 4.6; N, 5.3%.

 $W(N_2)(NCEt)(dppe)_2$ (I), obtained as dark red solid in 60% yield. *Anal*. Calc. for $C_{55}H_{53}N_3P_4W$: C, 62.1; H, 5.0; N, 3.9. Found: C, 61.9; H, 4.9; N, 3.8%.

 $W(N_2H_2)(NCEt)(dppe)_2(HSO_4)_2$ (II), obtained as white solid in 60% yield. *Anal*. Calc. for $C_{55}H_{57}N_3P_4S_2O_8W$: C, 52.4; H, 4.6; N, 3.3. Found: C, 49.7; H, 4.5; N, 2.9%. $W(N_2)(NCPr^n)(dppe)_2(HSO_4)_2$ (III), obtained as dark red solid in 50% yield. *Anal*. Calc. for $C_{56}H_{55}N_3P_4W$: C, 62.9; H, 5.6; N, 3.8. Found: C, 58.7; H, 5.3; N, 3.0%.

 $W(N_2H_2)(NCPr^n)(dppe)_2(HSO_4)_2$ (IV), obtained as light green solid in quantitative yield. *Anal*. Calc. for $C_{56}H_{59}N_3P_4S_2O_8W$: C, 52.3; H, 4.6; N, 3.3. Found: C, 52.3; H, 4.9; N, 3.0%.

 $W(N_2)(NCPh)(dppe)_2$ (V), obtained as dark green solid in 60% yield. *Anal*. Calc. for $C_{59}H_{53}N_3P_4W$: C, 63.7; H, 4.8; N, 3.8. Found: C, 63.4; H, 4.5; N, 3.2%.

2.1.1. IR spectroscopy

MIR spectra were obtained from KBr pellets using a Mattson Genesis Typ I spectrometer. FIR spectra were obtained from RbI pellets using a Bruker IFS 66 FTIR spectrometer. Both instruments were equipped with a Cryogenics helium cryostat. The spectra were recorded at 10 K and the resolution was set to 2 cm^{-1} .

2.1.2. Raman spectroscopy

Raman spectra were obtained on a Bruker IFS 66/CS NIR FT-Raman spectrometer at 270 K. The setup involves a 350 mW NdYAG-Laser with an excitation wavelength of 1064 nm. The samples were pressed into the groove of a holder which can be sealed with a glass plate to ensure inert gas conditions.

2.1.3. X-ray structure analysis

Intensity data were collected using a STOE Imaging Plate Diffraction System with Mo-K α radiation. The structure was solved with direct methods using SHELXS-97 [13]. Refinement was done against F^2 using SHELXL-97. All non-H atoms were refined anisotropically. In the subsequent refinement, the H atoms were positioned with idealized geometry and refined with isotropic displacement parameters using a riding model. Further information is contained in Table 1 and in the Supplementary Material.

2.1.4. Normal coordinate analysis

Normal coordinate calculations were performed using the QCPE computer program 576 by M.R. Peterson and D.F. McIntosh. It involves solution of the secular equation $GFL = \Lambda L$ by the diagonalization procedure of Miyazawa. The calculations are based on a general valence force field and the force constants are refined using the non-linear optimization routine of the simplex algorithm according to Nelder and Mead [14].

The QCA–NCA procedure [7d] is useful for the treatment of large molecules. If the real molecule M is too large to be handled completely with ab initio theory, a simplification is necessary. In the case of the complexes I and II, the substitution of the dppe ligands by PH₃ and the usage of molybdenum instead of tungsten leads to model complexes \tilde{I} and $I\tilde{I}$ (model \tilde{M}) which are suitable for DFT calculations. Frequencies and force

Table 1 Crystallographic data for [W(N₂)(NCEt)(dppe)₂]

Chemical formula Formula weight (g mol ⁻¹) Crystal colour Crystal system Space group a (Å) b (Å) c (Å) c (Å) α (°) β (°) γ (°) V (Å ³)	$\begin{array}{l} [W(N_2)(C_3H_5N)(C_{26}H_{24}P_2)_2] \\ 1063.73 \\ red \\ triclinic \\ P\overline{1} \\ 10.2526 (7) \\ 10.7823 (9) \\ 23.438 (2) \\ 87.73 (1) \\ 88.90 (1) \\ 64.96 (1) \\ 2345.6 (3) \\ 2 \end{array}$
D_{calc} (g cm ⁻³)	1.506
F(000)	1076
2θ -Range (°)	4-52
h/k/l Ranges	-11/12, -13/13, -28/28
$M (\mathrm{mm}^{-1})$	2.640
T (K)	150
Measured reflections	16915
Independant reflections	8477
R _{int}	0.0668
Refined parameters	569
Reflections with $F_{\rm o} > 4\sigma(F_{\rm o})$	6862
$R_1 \left[F_{\rm o} > 4\sigma \left(F_{\rm o} \right) \right]$	0.0417
WR_2 (all data)	0.0942
Goodness-of-fit	1.002
Residual electron density (e $Å^{-3}$)	1.564/-2.368

constants (matrix \tilde{f}) of model \tilde{M} have been calculated. In order to remove artificial interactions and to allow an easier handling, the H atoms of the PH₃ ligands were removed and the models $[W(N_2)(NCCH_3)(P)_4]$ (I') and $[W(NNH_2)(NCCH_3)(P)_4]^{2+}$ (II') were obtained. Truncation of the matrix \tilde{f} leads to matrix f' which can be divided into two parts: the force constants of the CH₃-C-N-W-N-N and the CH₃-C-N-W-N-NH₂ unit (core), respectively, and the force constants of the WP₄ unit (frame). Small non-diagonal elements were neglected. The force constants of the C-N-W-N-N and the C-N-W-N-NH₂ core were fit to the experimental frequencies. The force constants of the frame and those between core and frame were fixed at their theoretical values. Thus only selected force constants were refined in the QCA-NCA procedure.

2.1.5. DFT calculations

For the models \tilde{I} and $I\tilde{I}$ spin-restricted DFT calculations were performed using Becke's three parameter hybrid functional with the LYP correlation functional of Lee, Yang and Parr. The LanL2DZ basis set was used for the calculations. It applies Dunning/Huzinaga full double zeta (D95) [15] basis functions on the first row and Los Alamos effective core potentials plus DZ functions on all other atoms [16]. Charges were analyzed using the natural bond orbital (NBO) formalism [17]. All computational procedures were used as they are implemented in the GAUSSIAN-98 package [18]. Wavefunctions were plotted with the visualization program MOLDEN [19]. The force constants in internal coordinates were extracted from the GAUSSIAN output using the program REDONG [20]. The structures of the models \tilde{I} and $I\tilde{I}$ are fully optimized. The MO scheme of the NNH₂ ligand has been calculated as well using a fully optimized structure [7e]. For all model complexes, W has been substituted by Mo in order to simplify the calculations.

3. Crystal structure determination

The crystal structure of $W(N_2)(NCEt)(dppe)_2$ (I, Fig. 1) represents the first structural characterization of a tungsten(0) dinitrogen nitrile complex having a P_4 ligand set. The central tungsten atom is surrounded by one dinitrogen, one propionitrile and two bidentate bis(phosphine) ligands in a distorted octahedral geometry. The nitrile ligand occupies an axial position trans to the dinitrogen ligand. The N-W-N angle of 172.7 (2)° deviates slightly from linearity. The N-N distance of 1.120 (7) Å is somewhat longer than in free dinitrogen (1.0975 Å) [1c]. The elongation of the N-N distance is explained by back donation of electrons from the metal non-bonding d orbitals into antibonding π^* orbitals of dinitrogen. The two bis(phosphine) ligands are bound in equatorial position. The P-W-P bite angle is 80.97 (2) and 79.72 (5)°, respectively. The average P-W bond distance is 2.430 (2) Å. The average P-C bond distance of 1.861 (6) Å in the phosphine ligand of \mathbf{I} is slightly longer than in the uncomplexed ligand (1.821 and 1.818 Å, respectively) [21]. The W–N distances are 1.982 (5) Å for dinitrogen and 2.110 (4) Å for the nitrile nitrogen atom. The C-N distance in the nitrile ligand is 1.146 (7) Å. Relevant bond distances and angles are listed in



Fig. 1. Crystal structure of $[W(N_2)(NCEt)(dppe)_2]$ (I) with labeling and displacement ellipsoids drawn at the 50% probability level (the hydrogen atoms are omitted for clarity).

Table 2

Compariso	on of selected	experimental	and	calculated	bond	lengths	and
angles for	[W(N ₂)(NCE	t)(dppe) ₂]					

	Experimental	Calculated
Bond lengths (Å)		
N(1) - N(2)	1.120 (7)	1.170
N(1) - W(1)	1.982 (5)	1.993
W(1) - N(3)	2.110 (4)	2.098
W(1) - P(1-4)	2.419 (2) -2.450 (2)	~ 2.49
N(3) - C(5)	1.146 (7)	1.189
C(5) - C(6)	1.477 (8)	1.467
Bond angles (°)		
N(1) - W(1) - N(3)	172.7 (2)	178.6
N(2) - N(1) - W(1)	176.5 (5)	177.7
N(3) - C(5) - C(6)	175.6 (6)	179.2
C(5) - N(3) - W(1)	171.9 (4)	179.1
P(2)-W(1)-P(1)	80.97 (5)	89.4
P(3)-W(1)-P(4)	79.72 (5)	90.6

Table 2. Selected Crystallographic data are presented inTable 1.

The N-N distance of 1.120 (7) Å is of similar magnitude compared with that in the structures of $[W(N_2)_2(dppe)_2]$ (0) [22]. The W-N distance of I of 1.982 (5) Å is significantly shorter than in the first polymorph of 0, [22a] but comparable with those in the second one [22b]. The average W-P distances are comparable in all systems. All P-W-P angles deviate significantly from 90° present in an ideal octahedral environment.

4. Electronic structure

4.1. Input geometries and geometry optimizations

The structure of the model system \tilde{I} used for the calculation is derived from the crystal structure of complex I and is fully optimized. Experimentally determined bond lengths and angles are compared with calculated values (after optimization) in Table 2. In order to simplify the computational problem, the coordinating phosphorus donors were substituted by ideal PH₃ ligands in a geometry retrieved from literature data. The alkyl group of EtCN was substituted by NCCH₃. Input coordinates of \tilde{I} are collected in Table 3. The structure of model system II was derived from that of \tilde{I} by adding two hydrogen atoms to the N₂ group at a distance known from the NNH_2 complex [MoF(NNH₂)(dppe)₂](BF₄) [23]. Input coordinates are given in Table 4. Structure \tilde{V} was obtained from \tilde{I} by replacing the methyl group on the nitrile ligand by phenyl. Input coordinates are given in Table 5. All

Table 3 Coordinates of $[Mo(N_2)(NCCH_3)(PH_3)_4]$ (\tilde{I})

Atom	Position ^a	Position ^a							
	x	у	Ζ						
С	0.049	-4.473	0.000						
С	0.038	-3.006	0.000						
N	0.012	-1.817	0.000						
Мо	0.000	0.281	0.000						
Р	-2.507	0.314	0.000						
Р	0.025	0.255	2.495						
Ν	-0.059	2.273	0.000						
N	-0.139	3.440	0.000						
Р	2.487	0.308	0.000						
Р	0.025	0.255	-2.495						
Н	-0.934	1.000	3.286						
Н	1.185	0.698	3.245						
Н	-0.139	-0.995	3.213						
Н	3.236	0.933	-1.074						
Н	3.236	0.933	1.074						
Н	3.244	-0.930	0.000						
Н	1.185	0.698	-3.246						
Н	-0.139	-0.995	-3.213						
Н	-0.934	1.000	-3.286						
Н	-3.152	1.608	0.000						
Н	-3.313	-0.249	-1.067						
Н	-3.313	-0.249	1.067						
Н	-0.461	-4.869	0.888						
Н	-0.461	-4.869	-0.888						
Н	1.077	-4.858	0.000						

Table 4 Coordinates of $[Mo(N_2H_2)(NCCH_3)(PH_3)_4]$ ($\tilde{I}I$)

Atom	Position ^a			
	x	у	Ζ	
С	4.549	0.0046	-0.0347	
С	3.088	0.003	-0.0249	
N	1.913	-0.001	-0.0203	
Мо	-0.362	-0.006	-0.001	
Р	-0.191	-1.747	1.925	
Р	-0.108	1.957	1.714	
Р	-0.244	1.769	-1.907	
N	-2.133	-0.011	0.006	
N	-3.447	-0.012	0.011	
Р	-0.136	-1.963	-1.712	
Н	-1.082	2.917	-1.759	
Н	-0.582	1.400	-3.246	
Н	1.011	2.409	-2.144	
Н	-0.103	-3.316	-1.247	
Н	-1.172	-2.061	-2.689	
Н	1.011	-1.966	-2.563	
Н	-0.042	-3.136	1.614	
Н	0.857	-1.607	2.888	
Н	-1.319	-1.815	2.798	
Н	-1.233	2.166	2.567	
Н	0.931	1.865	2.690	
Н	0.105	3.297	1.260	
Н	4.929	0.996	-0.308	
Н	4.938	-0.258	0.957	
Н	4.926	-0.727	-0.760	
Н	-3.964	-0.298	-0.817	
Н	-3.957	0.269	0.845	

^a Coordinates of the atoms in Å.

structures were optimized. Relevant bond lengths of the optimized structures are indicated in Fig. 2.

4.2. Electronic structure of the N_2 complex with a trans alkyl nitrile ligand

The molecular orbital (MO) scheme of the Molybdenum N2 model complex with a trans acetonitrile ligand, I, is very similar to that of the Mo bis(dinitrogen) complex which we have studied earlier (Fig. 3) [7d,7e]. Charge decompositions and shapes of relevant orbitals are given in Table 6 and Fig. 4, respectively. The HOMO of \tilde{I} is contained within the twofold degenerate set of bonding combinations between the Mo d_{xz} and d_{vz} orbitals and the ligand (i.e. dinitrogen and nitrile) π_x^* and π_v^* orbitals, respectively. These combinations are designated $d_{xz} = \pi_x^*$ and $d_{yz} = \pi_y^*$. For both ligands, the contribution of the coordinating atom in these combinations (N_{α} for dinitrogen, N^{C} for nitrile) is very small relative to that of the β atom (N_{β} and C^N, respectively). The LUMO of \tilde{I} is part of the twofold degenerate set of non-bonding combinations of $\pi^*(NN)$ and $\pi^*(CN)$ orbitals in x- and y-direction, respectively. At much higher energy, finally, the antibonding combinations of ligand π^* orbitals with the metal d_{xz} and d_{yz} orbitals, $\pi_x^* d_{xz}$ and $\pi_y^* d_{yz}$, are found. This orbital pattern corresponds to $d_{\pi}(metal) \rightarrow \pi^*$ (ligand) back donation. $^{\rm a}\,$ Coordinates of the atoms in Å.

Notably, backbonding acts to put electron density primarily on the β atom of both ligands, and dinitrogen participates more than nitrile in the bonding combinations (about 15 vs. 9% orbital contribution for N–N and C–N, respectively).

Metal-ligand coordination is complemented by σ bonding. For the N₂ group this is mediated by the $p_{\sigma}(NN)_d_{z^2}$ orbital that is heavily admixed by phosphine functions and has metal d_{z^2} and N₂ contributions of about the same magnitude (15 and 24%, respectively, Fig. 4). The participation of the CN group in this orbital is weak. Nitrile σ bonding is primarily mediated by the $p_{\sigma}(CN)$ orbital that has a very high contribution of the CN group, especially at N^C (N^C: 56%, C^N: 17%). Furthermore, it has a 10% contribution of N₂ and a metal contribution of only 8% (Table 6). The $p_{\sigma}(NN)_p_{\sigma}(CN)_d_{z^2}$ orbital at low energy is a superposition of N₂ and nitrile σ orbitals (Fig. 4). As in the bis(dinitrogen) complex, π donation from the ligand π orbitals is found to be negligible.

Comparing the NPA charges on the two axial ligands of \tilde{I} (Table 7), it becomes apparent that the CN group in \tilde{I} carries a smaller negative charge (-0.05) than the dinitrogen ligand (-0.22). In particular, the negative charge on N_β is twice as large in \tilde{I} (-0.12) as in the

Table 5 Coordinates of $[Mo(N_2)(NCPh)(PH_3)_4]$ (\tilde{V})

Atom	Position ^a		
	x	У	Ζ
С	0.055	3.305	0.000
С	0.033	1.880	0.000
Ν	0.000	0.685	0.000
Мо	-0.016	-1.378	0.000
Р	0.007	-1.401	2.507
Р	-2.526	-1.353	0.000
Р	0.007	-1.401	-2.507
Ν	-0.095	-3.376	0.000
Ν	-0.195	-4.541	0.000
Р	2.474	-1.351	0.000
Н	-0.727	-2.408	-3.240
Н	1.239	-1.555	-3.256
Н	-0.481	-0.267	-3.262
Н	3.248	-1.937	1.075
Н	3.248	-1.937	-1.075
Н	3.162	-0.075	0.000
Н	1.239	-1.555	3.256
Н	-0.481	-0.267	3.262
Н	-0.727	-2.408	3.240
Н	-3.217	-2.621	0.000
Н	-3.305	-0.756	1.067
Н	-3.305	-0.756	-1.067
С	1.292	4.010	0.000
С	1.306	5.413	0.000
С	0.098	6.141	0.000
С	-1.132	5.450	0.000
С	-1.161	4.048	0.000
Н	2.224	3.451	0.000
Н	2.257	5.940	0.000
Н	0.115	7.228	0.000
Н	-2.066	6.006	0.000
Н	-2.109	3.518	0.000

^a Coordinates of the atoms in Å.

corresponding bis(dinitrogen) complex (-0.06) which is important to protonation. Consequently a higher amount of negative charge is transferred from the metal to the single N₂ ligand in \tilde{I} than to each of the two N₂ groups in the (N₂)₂ complex; i.e. the N₂ group in \tilde{I} is activated to a higher degree than each of the two groups of the bis(dinitrogen) system. Hence, nitrile must be a weaker π acceptor and/or a stronger σ or π donor than N₂. From the above observations, nitrile is in fact a weaker π acceptor than N₂. As in case of N₂, π donation from nitrile to the metal is very weak (note the very small metal contribution in the π_x , π_y orbitals being largely localized on N^C).

In addition, the nitrile ligand is found to be a weaker σ donor than dinitrogen. Upon going from N₂ to nitrile, one N atom is replaced by the weaker electronegative C-CH₃ group. This difference in electronegativity is the origin for the large polarization of the CN group leading to a charge of -0.40 at N^C and of +0.35 at C^N. However, this large amount of negative charge on N^C is



Fig. 2. Optimized structures for the model complexes.

not donated to the metal to a significant degree. The overlap between the C–N σ orbital $p_{\sigma}(CN)$ having lonepair character on N^C and the metal is even weaker than in case of the N₂ p_{σ} orbital. This probably derives from the fact that the coordinating nitrogen atom of the nitrile group is bound to a positively charged C atom and hence, cannot donate electron density to a significant extent (see below). To conclude, the primary bonding interaction for the nitrile group with the Mo/ W(0) center is backbonding, but is weaker than in the case of the N₂ ligand. For this reason, the dinitrogen systems with *trans* nitrile ligands should be thermodynamically less stable than their bis(dinitrogen) counterparts. This is also evident from the back transformation of the *trans* alkyl nitrile complexes **I**



Fig. 3. Orbital schemes of \tilde{I} and $\tilde{I}I$.

and III into the bis(dinitrogen) complex 0 at room temperature under N₂ (vide supra).

4.3. Electronic structure of the N_2H_2 complex $\tilde{I}I$

Addition of two protons to the dinitrogen complex \tilde{I} leads to the 'hydrazido(2-)' model compound $\tilde{I}I$ with a *trans* acetonitrile ligand which is related to the analogous intermediate with a *trans* fluoro ligand that has been characterized earlier [7d,7e]. Charge decompositions and shapes of relevant orbitals are given in Table 8 and Fig. 5, respectively. As in the case of the corresponding *trans* fluoro system, the non-bonding d_{xy} orbital is the HOMO of complex $I\tilde{I}$ (Figs. 3 and 5). Below the HOMO are the bonding combinations of d_{xz} and d_{yz} with the N₂H₂ π_h^* and π_v^* orbitals, respectively. The π^* orbital lying within the N₂H₂ plane, π_h^* , has

transformed into a π donor orbital at N_{α} , and the bonding combination of this orbital with d_{xz} primarily has ligand character. This corresponds to an effective transfer of about two electrons from the metal to the N₂ ligand, initiated by the double protonation reaction. In contrast, the bonding combination of $d_{\nu z}$ with the outof plane π^* orbital of the N₂H₂ group, π_v^* , still has predominantly metal character. The occupation of this orbital corresponds to back donation from $d_{\nu z}$. The LUMO contains the antibonding combination of d_{xz} with π_h^* . Importantly, this orbital still carries a bonding contribution of the nitrile π_x^* orbital, like in the parent complex \tilde{I} (Fig. 5). To higher energy, the antibonding combination of d_{yz} with the π_v^* orbital is found. The antibonding combinations of nitrile π_x^* and π_y^* functions with d_{xz} and d_{yz} , respectively, are located at still higher energy as shown in Fig. 3.

Orbital	Label	Energy (Hartree)	Charge	decomp	osition						
			% Mo	% P	% Ν ^α	$\% N^{\beta}$	% N ^C	% C ^N	% C	% H ^C	% H ^P
$\pi_x^*(NN)_\pi_x^*(CN)_d_{xz}$	<54>	0.0615	5	40	2	1	1	0	1	1	49
$\pi_v^*(NN)_\pi_v^*(CN)_d_{vz}$	(53)	0.0540	9	18	15	11	8	5	2	8	23
$\pi_x^*(NN)_\pi_x^*(CN)$	$\langle 52 \rangle$	0.0507	18	22	8	7	9	7	3	6	21
$\pi_v^*(NN)_\pi_v^*(CN)$	$\langle 43 \rangle$	0.0011	17	24	7	11	9	16	1	7	9
$\pi_x^*(NN)_\pi_x^*(CN)$	$\langle 42 \rangle$	0.0011	18	24	8	12	9	15	1	7	8
$D_{vz} \pi_v^*(NN) \pi_v^*(CN)$	$\langle 41 \rangle$	-0.1372	61	2	1	15	0	9	0	2	11
$D_{xz} \pi_x^*(NN) \pi_x^*(CN)$	$\langle 40 \rangle$	-0.1373	60	2	1	14	0	9	0	2	11
D_{xy}	$\langle 39 \rangle$	-0.1456	68	3	0	0	0	0	0	0	28
$\pi_x(CN)_{\pi_x(NN)}$	$\langle 38 \rangle$	-0.2812	7	77	1	2	2	2	0	0	10
$\pi_v(CN)_{\pi_v}(NN)$	$\langle 37 \rangle$	-0.2814	7	77	1	2	2	2	0	0	10
$\pi_{v}(CN)$	$\langle 35 \rangle$	-0.3460	2	4	0	0	49	27	6	5	6
$\pi_x(CN)$	$\langle 34 \rangle$	-0.3470	2	4	1	1	48	27	6	5	5
$p_{\sigma}(NN)_{d_{z^2}}$	$\langle 33 \rangle$	-0.3485	15	51	9	15	2	1	0	0	7
$p_{\sigma}(CN)$	$\langle 21 \rangle$	-0.4315	8	2	4	6	56	17	5	1	1
$p_{\sigma}(NN)_p_{\sigma}(CN)_d_{z^2}$	$\langle 17 \rangle$	-0.5392	7	1	51	20	8	7	4	1	0

Table 6 Charge contributions of $[Mo(N_2)(NCCH_3)(PH_3)_4]$ (\tilde{l})

P and H are the sums over all corresponding atoms.

To summarize, the characteristics of metal-N₂H₂ binding in II are very similar to those in the corresponding *trans* fluoro N₂H₂ complex. In both cases, the metal center can be assigned a formal charge of +II. Nitrile bonding in the N₂H₂ complex II, however, is very different from that present in the precursor I: while the nitrile group participates in backbonding in I, it has negligible contributions to the occupied orbitals with metal d character in II and, therefore, is practically nonbonding with its π_x^* and π_y^* orbitals. Considering the NPA charges on the nitrile group of II, it becomes apparent that the polarization of the CN group, which already is large in the uncoordinated ligand and in complex I, has further increased in II (N^C: -0.50, C^N: +0.56). Surprisingly, however, this does not lead to an increase of metal-nitrile σ bonding upon going from \tilde{I} to $\tilde{I}I$. The metal contribution to the orbital $p_{\sigma}(CN)_p_{\sigma}(NN)_d_{z^2}$ remains low (Fig. 5 and Table 8). As π donation is not increased either, the bonding between the nitrile group and the Mo center now becomes very weak. This is also reflected by a very large Mo-N(nitrile) bond length (calc. 2.275 Å after optimization, vs. 2.098 Å in I).

Comparing the charges on the N_2H_2 ligand between the *trans* fluoro and *trans* nitrilo complexes shows that the nitrilo complex $\tilde{I}I$ has a weaker activated N_2H_2 ligand than the corresponding fluoro compound (+0.20 vs. -0.03 total charge on N_2H_2 , cf. Table 7). This difference is obviously due to the different charges of the *trans* ligand. In [MoF(NNH₂)(PH₃)₄]⁺ the fluoro



Fig. 4. Important orbitals of \tilde{I} .

Table	7			
NPA	Charges	of different	Mo	complexes

Complex	Atom								
	Мо	N^{α}	N^{β}	Н	N ^c	C^N	<i>P</i>		
Free CH ₃ CN ligand					-0.37	0.33			
$[Mo(N_2)_2(PH_3)_4][7e]$	-1.01	-0.07	-0.06				0.31		
$[Mo(N_2)(NCCH_3)(PH_3)_4]$ (\tilde{I})	-0.89	-0.10	-0.12		-0.40	0.35	0.29		
$[Mo(N_2)(NCPh)(PH_3)_4](\tilde{V})$	-0.84	-0.09	-0.10		-0.39	0.34	0.29		
$[Mo(NNH_2)(NCCH_3)(PH_3)_4]^{2+}$ ($I\tilde{I}$)	-0.02	-0.10	-0.58	0.44	-0.50	0.56	0.20		
$[MoF(NNH_2)(PH_3)_4]^+$ [7e]	0.04	-0.21	-0.68	0.43			0.24		
$[MoF(NNH_3)(PH_3)_4]^2$ -[29]	0.19	-0.36	-0.60	0.48			0.20		

 N^{α} is the coordinating and N^{β} the terminal dinitrogen atom of N₂. N^c is the dinitrogen atom from the nitrile. \tilde{P} is the average of all P atoms.



Fig. 5. Important orbitals of $\tilde{I}I$.

ligand carries a negative charge of -0.55, i.e. has transferred 0.45 charge units to the MoNNH₂ fragment

Table 8 Charge contributions of $[Mo(N_2H_2)(NCCH_3)(PH_3)_4]^{2+}$ $(\tilde{I}I)$

[7d,7e]. These are missing in the case of the *trans* nitrile complex (the CN group carries a positive charge of + 0.06). We have pointed out earlier that the N₂H₂ ligand in the MoF(NNH₂) complex corresponds to neutral isodiazene and that the hydrazido(2-) formulation is misleading [7d,7e]. The same applies to the weaker activated N₂H₂ intermediate of the *trans* nitrile system.

4.4. Electronic structure of the N_2 complex with a trans benzonitrile ligand \tilde{V}

It has been found earlier that the N₂ complex can also be prepared with a *trans* benzonitrile ligand [8]. However, a corresponding N₂H₂ intermediate has not been described. It therefore appeared of interest to investigate the electronic-structural differences between dinitrogen complexes with alkyl nitrile and benzonitrile groups. Table 7 shows that in fact the negative charge on the N₂ ligand is slightly lower in the system coordinated by an aromatic nitrile than in a system with a *trans* aliphatic nitrile ligand. Fig. 6 shows the electronic structural origin of this difference: there is a delocalization of

Orbital	Label	Energy (Hartree)	Charge	decom	position							
			% Mo	% P	% Ν ^α	% N ^β	% N ^C	% C ^N	% C	% H ^C	% H ^P	% H ^N
$\pi_{n}^{*}(CN)_{\pi_{n}}^{*}(NN)_{d_{n}}$	<i><</i> 47 <i>></i>	-0.2421	14	1	8	2	29	34	1	11	1	0
$\pi_h^*(CN)_d_{yz}$	$\langle 46 \rangle$	-0.2469	11	4	2	1	29	36	0	11	2	3
$d_{\nu z} = \pi_{v}^{*}(CN) = \pi_{v}^{*}(NN)$	$\langle 43 \rangle$	-0.3077	25	10	31	13	3	11	0	2	4	0
$d_{yz} = \pi_h^*(CN)$	$\langle 42 \rangle$	-0.3348	47	9	23	0	1	8	0	1	4	6
d_{xv}	$\langle 41 \rangle$	-0.4588	88	0	0	0	0	0	0	0	12	0
$\pi_v^*(NN)_d_{vz}$	$\langle 40 \rangle$	-0.4890	43	0	10	42	0	2	0	0	2	0
$d_{xz} = \pi_h^*(NN)$	$\langle 37 \rangle$	-0.5732	23	10	53	4	0	0	0	0	4	7
$\pi_v(CN)$	$\langle 34 \rangle$	-0.6216	2	3	0	0	45	19	18	10	4	0
$\pi_h(CN)$	$\langle 33 \rangle$	-0.6227	2	4	0	0	45	18	18	10	4	0
$\pi_v(NN)$	$\langle 31 \rangle$	-0.6527	2	23	21	24	1	0	1	0	28	0
$\pi_v(NN)$	$\langle 25 \rangle$	-0.6764	3	46	4	3	0	0	0	0	43	0
$\pi_v(NN)_d_{vz}$	$\langle 24 \rangle$	-0.6772	7	18	31	23	0	0	2	1	16	0
$p_{\sigma}(CN)_p_{\sigma}(NN)_d_{z^2}$	$\langle 23 \rangle$	-0.7066	9	2	6	4	45	17	8	1	2	0
$p_{\sigma}(CC)_p_{\sigma}(NN)_d_{z^2}$	$\langle 20 \rangle$	-0.7620	8	0	7	9	6	22	27	6	0	1

P and H are the sums over all corresponding atoms.



Fig. 6. Important orbital of \tilde{V}

charge from the backbonding d_{yz} orbital into the π^* system of the aromatic ring such that the charge transfer into the N₂ π_v^* orbital is lowered. This reduction of negative charge is obviously sufficient to prevent protonation of the coordinated N₂ ligand.

5. Vibrational spectra and QCA-NCA

5.1. Vibrational spectra of $[W(N_2)(NCEt)(dppe)_2]$ (I)

The Raman spectra of I (Fig. 7) exhibit two peaks at 1897 and 462 cm⁻¹ that shift in the ¹⁵N₂-substituted compound. The signal at 1897 cm⁻¹ shifts by about 60 cm⁻¹ down to 1834 cm⁻¹ and is assigned to the N–N stretching vibration. The peak at 462 cm⁻¹ shifts by 18 cm⁻¹ on ¹⁵N substitution and is assigned to the W–N

stretching vibration between tungsten and N_2 , v(WN). In the ¹⁴N compound, the v(WN) peak overlaps with another signal which is the reason for the appearance of two peaks in the ¹⁵N spectra. The unshifted peak cannot be assigned. It is neither the v(WN) stretch of the nitrile (based on the frequency predicted from the calculations, vide infra), nor does it originate from a splitting of the former vibration. Other intense features in the Raman spectra which remain unshifted in the ¹⁵N compound are found at 2185, 1584, 1028, 1093, 999, 525 and 178 cm^{-1} . The signal at 2185 cm^{-1} is assigned to the C-N stretching mode v(CN) of the nitrile and the peak at 178 cm^{-1} to the symmetric W–P stretch v(WP). Comparison with data from $[W(N_2)_2(dppe)_2]$ suggests that the remaining vibrations are due to the phenyl residues of the dppe ligand: thus, the peak at 1586 cm^{-1} belongs to a C=C stretch; 1093 and 1028 cm⁻¹ are the in-plane bending vibrations $\delta(CCC)$ and $\delta(CCH)$, and the feature at 525 cm^{-1} is either an out-of-plane bend γ (CCC) or the P-phenyl stretch [24].

The infrared spectra of complex I are given in Fig. 8. Besides the N–N stretching vibration v(NN) at 1897 cm⁻¹ which shifts to 1836 cm⁻¹ on ¹⁵N substitution, another isotope sensitive band is found below 600 cm⁻¹. The band at 555 cm⁻¹ is assigned to the δ (WNN) bend and shifts by about 17 cm⁻¹ into a broad feature. The other isotope sensitive signals at 2010 and 1947 cm⁻¹ in the ¹⁴N spectra (¹⁵N: 1958 and 1881 cm⁻¹) are due to



Fig. 7. Raman spectra of [W(N₂)(NCEt)(dppe)₂] (I).



Fig. 8. IR spectra of [W(N₂)(NCEt)(dppe)₂] (I).

the symmetric and antisymmetric NN vibrations of the precursor $[W(N_2)_2(dppe)_2]$ (0). The v(CN) stretching mode is found at 2190 cm⁻¹. The observed signals at 1585, 1093, 1026 and 1000 cm⁻¹ are assigned as presented above. Frequencies and assignments are collected in Table 9.

5.2. QCA-NCA of $[W(N_2)(NCEt)(dppe)_2]$ (I)

The structure of model system $[W(N_2)(NCCH_3)(P)_4]$ (I') used for the normal coordinate analysis is shown in Fig. 9. The QCA–NCA procedure is performed as described in the experimental section. The v(NN), v(CN), $\delta(WNN)$, and v(WN) vibrations are fit to the experimental data. Table 9 shows the comparison between the experimentally determined peak positions, the calculated data retrieved from DFT (B3LYP) and the QCA-NCA results. The *f*-matrix for the relevant C-N-W-N-N core is shown in Table 10.

The agreement between the DFT results and the experiment is good. The v(CN) stretch is found between 2185 and 2190 cm⁻¹ and is calculated to be at 2199 cm⁻¹. The v(NN) stretch is calculated by DFT to 1957 cm⁻¹, but is found at 1897 cm⁻¹. For the bending mode δ (WNN) only one signal at 555 cm⁻¹ is observed (see Table 9) although calculations indicate a splitting into two signals at 555 cm⁻¹ and 393 cm⁻¹. This could not be confirmed by experimental data. The v(WN) stretch

Mode Experimental			QCA-NCA	B3LYP	
	$^{14}N (cm^{-1})$	$^{15}N (cm^{-1})$	$^{14}N (cm^{-1})$	$^{15}N (cm^{-1})$	$^{14}N_{Calc} (cm^{-1})$
v(CN)	2190/2185 ^a	2190/2185 ^a	2190	2190	2199
v(NN)	1895/1897 ^a	1836/1834 ^a	1897	1837	1957
δ (WNN)	555	538	555, 376	537, 364	555, 393
$v(WN^N)$	462 ^a	444 ^a	462	448	438
v(WN ^C)	n.o.	n.o.	270	269	285

Table 9 Comparison of the observed and calculated frequencies of $[W(N_2)(NCEt)(dppe)_2]$

n.o., not observed.

^a Raman-data, unlabeled data are IR-data.



Fig. 9. Structure of model system I'.

is found at 462 cm⁻¹ while the B3LYP calculations predict this vibration at 438 cm⁻¹, showing a deviation of 24 cm⁻¹. The ν (WN) stretch for the nitrile is not observed in the spectra, but the DFT calculations predict the signal at 285 cm⁻¹.

Comparison of the experimental data and the QCA– NCA result shows excellent agreement as given in Table 9. For the bending mode δ (WNN) only one signal at 555 cm⁻¹ could be observed experimentally. After fitting to the experimental data, the observed isotope shift as well as the ¹⁴N frequency are reproduced (see Table 9). The second signal is then predicted by QCA– NCA to be at 376 cm⁻¹ in the ¹⁴N complex and 364 cm⁻¹ in the isotope substituted compound. The ν (WN) stretch for the nitrile is not observed in the spectra but predicted after QCA–NCA to be located at 270 cm⁻¹.

The calculated force constants for I' are collected in Table 12. The force constant of the N–N stretch is 14.95 mdyn Å⁻¹, which reflects the activation of the dinitrogen in the complex compared with the free N₂ molecule (22.42 mdyn Å⁻¹) [7d]. Importantly, this value is lower than in the corresponding bis(dinitrogen) complex which has an $f_{\rm NN}$ value of 16.43 mdyn Å⁻¹. The CN force constant of the coordinated nitrile (16.70 mdyn Å⁻¹) is somewhat lower than in the free nitrile (17.01 mdyn Å⁻¹ calculated by DFT), showing a weak effect of backbonding. The force constant for the v(WN) stretch between tungsten and dinitrogen is 3.15 mdyn

Table 10 f Matrix of the central C-N-W-N-N unit in [W(NCCH₃)(N₂)(P₄)]

 \AA^{-1} (bis(dinitrogen) complex: 2.66 mdyn \AA^{-1}), and that of the corresponding bending vibration δ (WNN) 1.01 mdyn \AA^{-1} . The force constant of the v(WN) stretch between tungsten and the nitrile is 1.53 mdyn \AA^{-1} , which is much lower than that of the corresponding W-N₂ stretch. This again reflects the weak interaction between the metal and the nitrile ligand.

5.3. Vibrational spectra of $[W(N_2H_2)(NCEt)(dppe)_2][HSO_4]_2$ (II)

Due to fluorescence, the Raman spectra of **II** could not be obtained. Overview IR spectra are shown in Fig. 10; selected features are presented in Fig. 11. The IR spectra exhibit a very broad feature between 2700 and 3300 cm⁻¹ which is caused by the counterion and overlaps with the v(NH) vibrations. These are observed at 3329 and 3213 cm⁻¹, shifting to about 3279 (broad band) and 3181 cm⁻¹ on ¹⁵N isotope substitution. Other isotope sensitive signals are found at 1617 cm⁻¹ and at about 440 cm⁻¹. Both show very small shifts and are assigned to δ (NNH) and δ (WNN), respectively. The v(WN) stretch is masked by the broad band from the HSO₄⁻ counterion at about 590 cm⁻¹. The v(CN)stretch is found between 2262 and 2267 cm⁻¹ (see Table 11), and shows a shift to higher wavenumbers as compared with the free nitrile.

5.4. QCA-NCA of $[W(N_2H_2)(NCEt)(dppe)_2][HSO_4]_2$ (II)

The structure of model system $[W(N_2H_2)(NCCH_3)-(P)_4]$ (II') used for normal coordinate analysis is shown in Fig. 12; the QCA–NCA procedure is performed as described in the Experimental section. The v(NN), v(CN), $\delta(NNH)$, v(NH) and $\delta(WNN)$ vibrations are fit to the experimental data and comparison of the experimental data, the QCA–NCA fit and the predicted vibrational energies (from DFT) are shown in Table 11.

The DFT calculations predict all vibrations of this system at higher frequencies than measured experimentally. The two NH stretching modes (symmetric and antisymmetric) are calculated at 3671 and 3523 cm⁻¹ in

v(NN)	$v(WN^N)$	$v(WN^C)$	v(CN)	δ^x (WNN)	$\delta^{x}(\text{CNW})$	$\delta^{y}(WNN)$	$\delta^{y}(\text{CNW})$
f1							
f9	f2						
0	f10	f3					
0	0	f11	f4				
0	0	0	0	f5			
0	0	0	0	0	f6		
0	0	0	0	0	0	f7	
0	0	0	0	0	0	0	F8



Fig. 10. IR spectra of [W(NNH₂)(NCEt)(dppe)₂][HSO₄]₂ (II).



Fig. 11. Selected IR spectral features of II along with ¹⁵N substitution data (left: v(NN), middle: v(WN) (masked), right: $\delta(WNN)$). Arrows indicate positions of ¹⁵N shifted peaks.

Mode	Experimental		QCA-NCA	B3LYP	
	$^{14}N (cm^{-1})$	$^{15}N (cm^{-1})$	$^{14}N (cm^{-1})$	$^{15}N (cm^{-1})$	$^{14}N_{Calc} (cm^{-1})$
v _{as} (NH)	3329	3309	3313	3302	3671
$v_{\rm s}(\rm NH)$	3215	3194	3230	3225	3523
v(CN)	2263	2263	2261	2261	2299
δ (NNH)	1617	1614	1617	1614	1673
v(NN)	n.o.	1384	1428	1382	1500
$v(WN^N)$	~ 590	~ 590	592	576	634
δ (WNN)	~ 440	~ 440	446	442	448
$v(WN^{C})$	n.o.	n.o.	221	220	204

Table 11 Comparison of the observed and calculated frequencies of $[W(N_2H_2)(NCEt)(depe)_2][HSO_4]_2$

n.o., not observed.



Fig. 12. Structure of model system II'.

the ¹⁴N compound but observed at 3329 and 3215 cm⁻¹. v(CN) is found experimentally at 2263 and calculated at 2299 cm⁻¹. For the δ (NNH) bending mode, a difference of 56 cm⁻¹ between 1673 cm⁻¹ (calculated by DFT) and 1617 cm⁻¹ (observed) is obtained (Table 11). The position of the ¹⁴N v(NN) stretch which is masked by a broad feature was determined based on the position of the ¹⁵N peak. In the ¹⁵N spectra the v(NN) signal is observed at 1382 cm⁻¹ and calculated to be at 1500 cm⁻¹. Based on the DFT results, the tungsten dinitrogen stretch should be found at 634 cm⁻¹ but is masked in experiment by a band of the counterion (vide supra). The tungsten nitrile stretch is calculated at 204 cm⁻¹ but is not observed experimentally (Table 11). The δ (WNN) stretch was identified at about 440 cm⁻¹, based on the DFT prediction (448 cm⁻¹).

After QCA–NCA good agreement between experimental and theoretical values is achieved as shown in Table 11 The two NH stretching modes (symmetric and antisymmetric) are fit by QCA–NCA to 3313 and 3230 cm⁻¹ in the ¹⁴N compound and the ¹⁵N shifts are –11 and -5 cm⁻¹, respectively; somewhat smaller than obtained experimentally (–20 and –19 cm⁻¹). The position of the ¹⁴N ν (NN) stretch which is masked by a

broad feature was determined based on the position of the ¹⁵N peak. In the ¹⁵N spectra the v(NN) signal is observed at 1382 cm⁻¹. Based on QCA–NCA the ¹⁴N v(NN) stretch should be found at 1428 cm⁻¹ (cf. Table 11). The tungsten dinitrogen stretch is predicted at 592 cm⁻¹ for ¹⁴N by QCA-NCA, but is masked experimentally by a band of the counterion (vide supra). The tungsten nitrile stretch, finally, is calculated at 220 cm⁻¹ but is not observed (Table 11). The δ (WNN) stretch was identified at about 440 cm⁻¹, based on QCA–NCA (446 cm⁻¹ (¹⁴N)/442 cm⁻¹ (¹⁵N)), respectively.

The f-Matrix for the C–N–W–N–NH₂ core is shown in Table 13. Important calculated force constants for **I**' are collected in Table 12. The NN stretch has a diagonal force constant of 7.60 mdyn Å⁻¹. This is reduced compared with free NNH₂ (calculated 11.66 mdyn Å⁻¹), but higher than in [MoF(NNH₂)(dppe)₂](BF₄) (7.197 mdyn Å⁻¹) [7d]. The force constant for the CN stretch is with 17.60 mdyn Å⁻¹ larger than in the free ligand (17.01 mdyn Å⁻¹) or in **I** (16.70 mdyn Å⁻¹, vide supra). The force constants for the NH stretches are 5.90 and for the ν (WN) stretches 6.44 (between tungsten and dinitrogen) and 0.88 mdyn Å⁻¹ (between tungsten and nitrile), respectively. The value of the force constant for the δ (WNN) bend is 0.46 mdyn Å⁻¹.

5.5. Vibrational spectra of $[W(N_2)(NCPr^n)(dppe)_2]$ (III)

The vibrational properties of **III** are similar to those of **I**. The Raman spectrum of **III** exhibits three isotope sensitive peaks at 1893 shifting to 1830 on ¹⁵N-substitution, at 449 cm⁻¹ shifting by 22 to 427 cm⁻¹ and a weak signal at 2017 shifting to 1949 cm⁻¹ (Fig. 13). The peak at 1893 cm⁻¹ is assigned to v(NN) and the peak at 449 cm⁻¹ to v(WN). In the ¹⁴N compound, the v(WN) peak overlaps with another signal which is the reason for the appearance of two peaks in the ¹⁵N spectra (vide supra). The features at 2017 cm⁻¹ in the ¹⁴N spectra and at 1949 cm⁻¹ in the ¹⁵N spectra are assigned to the

Table 12		
Calculated force constants for	$[W(N_2)(NCEt)(PH_3)_4]$ (I') and	$[W(N_2H_2)(NCEt)(PH_3)_4]^{2+}$ (II')

Force constant	Free N ₂ [7d]	Free CH ₃ CN	$[W(N_2)(NCC_2H_5)(dppe)_2]$	$\left[W(N_{2}H_{2})(NCC_{2}H_{5})(dppe)_{2}\right]^{2+}$	Free NNH ₂ [30]
v(NN)	22.42		14.95	7.60	11.66
v(CN)		17.01	16.70	17.60	
δ (WNN)			1.01	0.46	
$v(WN^N)$			3.15	6.44	
$v(WN^{C})$			1.53	0.88	
$v_{as}(NH)$				5.90	5.89/4.61
$v_{s}(NH)$				5.90	

Units are mdyn/Å⁻¹ for stretching and mdyn \cdot Å⁻¹ for bending.

precursor, showing that the exchange reaction between nitrile and N_2 is not totally complete.

The IR spectrum of III (Fig. 14) is very similar to that of I. Isotope sensitive signals are found at 1895 cm⁻¹, shifting to 1826 on ¹⁵N substitution, and at 553 cm⁻¹, shifting by 5–548 cm⁻¹. They are assigned to ν (NN) and δ (WNN), respectively. The features at 1583, 1093, 1026, 1000, 530 and 179 cm⁻¹ are assigned as in I. The nitrile C–N stretch is found at 2171 cm⁻¹. The bands at 1944 and 2015 cm⁻¹ (¹⁴N) as well as the bands at 1955 and 1877 cm⁻¹ in the ¹⁵N spectra are caused by the precursor. Frequencies and assignments are collected in Table 14.

5.6. Vibrational spectra of $[W(N_2H_2)(NCPr^n)(dppe)_2][HSO_4]_2$ (IV)

The Raman spectra of **IV** are obscured by fluorescence such that no spectroscopic information could be obtained. The IR spectra exhibit a very broad feature between 2700 and 3300 cm⁻¹ which is caused by the counterion and overlaps with the ν (NH) vibrations. These are observed at 3321 and 3215 cm⁻¹, shifting to about 3309 (broad band) and 3194 cm⁻¹ on ¹⁵N isotope substitution, respectively. Other isotope sensitive signals are found at 1604 cm⁻¹ shifting to 1601 cm⁻¹ and at about 440 cm⁻¹ showing a very small shift, which are assigned to δ (NNH) and δ (WNN), respectively. The ν (WN) stretch is most probably



Fig. 13. Raman spectra of [W(N₂)(NCPrⁿ)(dppe)₂] (III).

v(NN)	$v(WN^C)$	v(CN)	$v(WN^N)$	v(NH)	v(NH)	$\delta^{x}(NNH)$	$\delta^{y}(NNH)$	$\delta^{x}(WNN)$	γ (NNHH)	$\delta^{y}(CNW)$	$\delta^{y}(WNN)$	τ (MoN)	τ (MoC)
f1													
0	f2												
0	f20	f3											
f15	f21	0	f4										
f16	0	0	0	f5									
f17	0	0	f22	0	f6								
f18	0	0	0	0	f24	f7							
f19	0	0	0	f23	0	f25	f8						
0	0	0	0	0	0	0	0	f9					
0	0	0	0	0	0	0	0	0	f10				
0	0	0	0	0	0	0	0	0	0	f11			
0	0	0	0	0	0	0	0	0	0	0	f12		
0	0	0	0	0	0	0	0	0	0	0	0	f13	
0	0	0	0	0	0	0	0	0	0	0	0	0	f14



Fig. 14. IR spectra of [W(N₂)(NCPrⁿ)(dppe)₂] (III).

Mode	$[W(N_2)(NCPr^n)]$	dppe)2]	[W(N ₂)(NCPh)(dppe) ₂]	
$[W(N_2)(N_2))$	NCPh)(dppe) ₂]			
Observed	l frequencies	of	$[W(N_2)(NCPr^n)(dppe)_2]$	and
Table 14				

	$^{14}N (cm^{-1})$	$^{15}N (cm^{-1})$	$^{14}N (cm^{-1})$	$^{15}N (cm^{-1})$
$ \frac{v(CN)}{v(NN)} \\ \frac{\delta(WNN)}{v(WN^{N})} $	2171/2171 ^a	2181/2171 ^a	2094	2090
	1895/1893 ^a	1826/1830 ^a	1919	1855
	553	548	540	Schulter 530
	449 ^a	427 ^a	n.o.	n.o.

n.o., not observed.

^a Raman-data, unlabeled data are IR-data.

masked by the broad band from the HSO_4^- counterion at about 590 cm⁻¹. The ν (CN) stretch is found between 2263 and 2265 cm⁻¹ (see Table 15), showing a shift to higher wavenumbers as compared with the free nitrile.

5.7. Vibrational spectra of [W(N₂)(NCPh)(dppe)₂] (V)

This compound loses dinitrogen on irradiation with laser light and thus only IR data could be obtained (Fig. 15). Intense features are found in the 14 N spectra at 3049, 2094, 1951, 1582, 1088 and 1026 cm⁻¹ which are

Table 15 Observed frequencies of [W(N₂H₂)(NCPrⁿ)(dppe)₂][HSO₄]₂

Mode	$[W(N_2N_2)(NCC_3H_8)(dppe)_2]$				
	$^{14}N (cm^{-1})$	$^{15}N (cm^{-1})$			
v _{as} (NH)	3321	3309			
$v_{\rm s}(\rm NH)$	3215	3194			
v(CN)	2263/2263 ^a	2265/2263 ^a			
$\delta_{s}(NNH)$	1604	1601			
$v(WN^N)$	~ 590	~ 590			
v(NN)	n.o.	1384			
δ (WNN)	~ 440	~ 440			

n.o., not observed.

^a Data from Raman, unlabeled data are IR-data.

assigned as in the case of compound I (see above). Isotope sensitive signals were found at 1919, assigned as v(NN), and at 540 cm⁻¹ (broad shoulder), assigned to $\delta(WNN)$. They shift by 64 cm⁻¹ (v(NN)) and 11 cm⁻¹ ($\delta(WNN)$) to lower wavenumbers on ¹⁵N substitution, respectively (cf. Table 15). The band at 3049 cm⁻¹ is assigned to v(CH), that at 2090 cm⁻¹ to v(CN). Bands at 1582, 1088 and 1026 cm⁻¹ are assigned as in compound I. The features at 1951 (¹⁴N) and 1886 cm⁻¹ (¹⁵N) correspond again to the NN- stretch of the precursor (vide supra).



Fig. 15. IR spectra of [W(N₂)(NCPh)(dppe)₂] (V).

6. Discussion and conclusions

In the preceding sections the electronic and vibrational structure descriptions of dinitrogen and diazenido(2-) complexes with trans nitrile ligands have been developed. Due to the fact that protonation of the dinitrogen complex with a trans nitrile group to the corresponding N₂H₂ complex proceeds under retention of this axial ligand, these systems appear to be particularly attractive candidates for the metal-centered catalysis of N_2 fixation. In contrast, one of the two dinitrogen ligands in the usual bis(dinitrogen) Mo and W systems is exchanged by a Lewis base deriving from the acid used for protonation, leading to a trans halide, hydrogen sulfate or sulfonic acid Mo/W-N₂H₂ complex [5]. This exchange of the axial ligand is unfavorable with respect to the realization of a catalytic cycle for nitrogen fixation (cf. Section 1).

Most importantly, the activation of the single N_2 group bound in *trans* position to nitrile is found to be higher than that of each of the two N_2 ligands in the corresponding bis(dinitrogen) system. This is evidenced by an increased electronic charge on the N_β atom of the N_2 group in the *trans* nitrilo as compared with the *trans* bis(dinitrogen) complex (-0.12 vs. -0.06). As a consequence, the protonation leading to the N_2H_2 complex

is more favorable in the trans nitrilo complex. Likewise, the N-N stretching frequency in the trans nitrilo system $[W(N_2)(NCEt)(dppe)_2]$ (I) of 1895 cm⁻¹ has a lower value than that in the bis(dinitrogen) complex $[W(N_2)_2(dppe)_2]$ (0) (2007 cm⁻¹ for the symmetric and 1954 cm^{-1} for the antisymmetric combination of the N-N stretches). This is also reflected by the obtained force constants: for the nitrilo complex, the QCA-NCA procedure gives an $f_{\rm NN}$ value of 14.95 mdyn Å⁻¹ which is lower than 16.43 mdyn $Å^{-1}$ calculated for the corresponding bis(dinitrogen) complex. Both, the transfer of electronic charge to N_{β} and the lowering of the N-N force constant with respect to the free ligand are due to backbonding into the π^* orbitals of dinitrogen. In agreement with the above findings, this interaction is found to be stronger in the DFT calculations for the single N₂ group in the *trans* nitrilo system than for each of the N_2 ligands in the bis(dinitrogen) complex. The stronger activation of the single N₂ group in I is also evident from the shorter W-N distance found in the crystal structure (1.983 Å in I vs. 2.004 Å in 0).

To a certain extent, the nitrile group competes with the *trans* dinitrogen ligand for back donation from the Mo/W(0) center: for all *trans* nitrilo dinitrogen systems, the C–N stretching frequency is found to be lower than in the corresponding free nitrile (EtCN: 2190 vs. 2249 cm⁻¹; iPrCN: 2171 vs. 2245 cm⁻¹, PhCN: 2094 vs. 2231 cm⁻¹) [8]. Nevertheless, the nitriles are weaker π acceptors than N₂. This is evidenced by a smaller lowering of the stretching frequency of the coordinated nitrile with respect to the free ligand (lowering of v(CN)) $60-75 \text{ cm}^{-1}$) than in the case of dinitrogen (lowering of v(NN) upon coordination over 400 cm⁻¹). Likewise, there is less negative charge on the C-N as compared with the N–N group (-0.05 vs. -0.22). Remarkably, the lower extent of backdonation is not compensated by stronger σ donation from nitrile; in contrast, this ligand is also found to be a weaker σ donor than N₂. This probably derives from the fact that σ donation from the nitrile p_{σ} orbital is limited due to the bonding of a positively charged C atom (see below). Taken together, these observations indicate that the bonding of nitriles to the Mo/W(0) center is much weaker than that of the N₂ group. The lability of the metal-nitrile bond is also evidenced by the thermally allowed transformation of the trans nitrile systems into their bis(dinitrogen) counterparts. On the other hand, the lower extent of backdonation into the nitrile π^* orbitals, is the origin for the higher activation found for the single dinitrogen group in the trans nitrilo complex as compared with that of each of the N₂ ligands in the bis(dinitrogen) system.

The dinitrogen complex with a trans PhCN ligand has a weaker activated N₂ group than the corresponding trans alkyl nitrile systems. This is evident from the higher N–N stretching frequency (1919 cm⁻¹) and from a slightly lower electronic charge calculated for the N_2 group. Nevertheless, the lowering of the C–N stretching frequency upon coordination of the free ligand to the metal center is largest for this group (137 vs. about 70 cm^{-1} for the alkyl nitriles; vide supra). The electronic reason for these observations is the delocalization of electronic charge from the d orbitals of the metal into the π^* orbitals of the aromatic nitrile ligand which acts to diminish the charge transfer to the N_2 group. The lower activation of the N2 ligand trans to the PhCN group as compared with systems with trans alkyl nitrile ligands is in agreement with trends obtained from electrochemical oxidation potentials [9].

The second important result of the spectroscopic investigations and DFT calculations is the fact that the activation of the NNH₂ group with a *trans* nitrilo ligand is lower than in corresponding NNH₂ systems having *trans* halide ligands. This is evidenced by the positive charge on this group in the NNH₂-nitrile complex (+0.20), while the corresponding *trans* fluoro-NNH₂ system has an almost neutral NNH₂ ligand (charge -0.03). Clearly, the hydrazido(2-) formulation is even less appropriate for the description of the NNH₂ group in the *trans* nitrile than in the *trans* fluoro complex. In addition, the N-N stretching frequency is higher for the nitrilo-NNH₂ ($v(^{15}N-^{15}N)$: 1384 cm⁻¹) compared with the fluoro NNH₂ system ($v(^{15}N-^{15}N)$: 1343 cm⁻¹; the

corresponding ${}^{14}N-{}^{14}N$ stretch is obscured in the nitrilo complex), indicating a lower degree of backbonding.

The origin for the lower activation of NNH₂ trans to nitrile as compared with trans halide is the fact that nitrile is a neutral ligand while a trans halide ligand is able to donate additional electron density into the Mo/ W–NNH₂ moiety. In the trans fluoro complex, the F ligand is assigned an NPA charge of -0.55, i.e. has transferred 0.45 charge units to the Mo/W complex. In contrast, the C–N group of the nitrile ligand acquires a total charge of +0.06 at the NNH₂ stage, practically the same value as in the N₂ complex (vide supra). Hence, in the case of nitrile there is no synergetic effect to the protonation process due to donation from the trans ligand. Nevertheless the example of the nitrile systems demonstrates that protonation of an N₂ complex is possible without exchange of the trans axial ligand.

It has been found by ¹⁵N NMR spectroscopy that the shielding of N_{α} and N_{β} in the NNH₂ ligand as a function of the *trans* ligand decreases in the sequence halide > $HSO_4^- > NCPr^n$ [10]. The weaker shielding (or stronger deshielding) of NNH₂ in the *trans* HSO_4^- complex as compared with trans halide systems has been suggested to be associated with a movement of electronic charge towards the trans NNH₂ group which then should be more susceptible to protonation than in the case of the trans halide systems [25]. From the above trend of the N_{α} and N_{β} chemical shifts, this should be even more pronounced for the trans NCPrⁿ complex, i.e. this complex should have the *highest* activated NNH₂ ligand. Our results indicate that the opposite is the case. Therefore, the shielding of N_{α} and N_{β} and activation of the NNH₂ ligand have to go in parallel. This would also be in agreement with the stronger shielding of N_{α} and N_{β} observed for W than for Mo/N₂ and $-N_2H_2$ complexes corresponding to a higher activation of NNH₂ and N₂, respectively [10,26]. As a consequence, however, the activation of NNH₂ in the trans HSO₄⁻ complex would be lower than in trans halide systems. This would correspond to the weaker Lewis basicity of HSO_4^- as compared with halide, again reflecting the influence of the donor properties of the trans ligand on the activation of the N₂H₂ group.

Remarkably, the bonding of the nitrile group which has been found to be weak in the case of the N₂ complex (vide supra), becomes even weaker in the NNH₂ complex. The calculations show that nitrile is in fact a very weak ligand at this stage of N₂ reduction. There is no backbonding into nitrile π^* orbitals any more. Neither is nitrile bound by a significant σ donor interaction to the metal center. This is illustrated by the large Mo–N(nitrile) bond distance (2.275 Å) and the short C–N bond distance (calc. 1.175 vs. 1.189 Å in the free nitrile). In the N₂H₂ complex there is a further increase of the polarization of the C–N group which already has been strong in the *trans* dinitrogen complex. However, the negative charge at the nitrile N atom is not transferred to the metal to a significant degree. A possible explanation for this observation is provided by the fact that the nitrogen donor of the nitrile group is bound to a positively charged C atom and hence, cannot act as a strong donor.

This bonding description is also supported by the results of vibrational spectroscopy. In contrast to the *trans* dinitrogen complexes where the C–N stretching frequencies have been found to be lowered with respect to the free ligands (vide supra), they are shifted to higher values in the NNH₂ system. This increase of the C–N stretching frequency which is also observed for other nitrile complexes [8] is obviously correlated to a shortening of the C–N bond occurring as a result of the increase of polarization of the C–N unit upon bonding to a metal center. Only in the case of coordination to an electron-rich metal, this effect is overcompensated by backbonding leading to a lowering of the C–N stretching frequency with respect to the free ligand, as observed in the case of the Mo/W(0) nitrile systems.

This finding bears an interesting relationship to the theoretical results of Frenking et al. on the properties of CO coordinated to metal centers [27]. Here, the C-O triple bond also becomes shorter when the metal cation approaches the carbon atom; only at the onset of metal \rightarrow CO back donation this trend is reversed, and the C-O bond becomes longer again. With respect to the polarization of the coordinating group, however, there is a remarkable difference between CO and RCN: upon coordination of a metal or H^+ to the C atom of CO, the polarization between C and O is found to decrease whereas in the case of a metal coordinating to the N atom of the nitrile ligand, the polarization between N and C is found to increase (vide supra). This difference is certainly due to the fact that in the case of CO the less electronegative atom acts as a σ donor to the metal while in case of RCN this function is located at the more electronegative atom.

What are the consequences of the above results with respect to the rational design of metal complexes able to catalyze N₂ fixation? As a first application, nitrile groups have been used to attach Mo/W dinitrogen complexes with equatorial phosphine ligands to electrodes [11]. In this geometry, the nitrile ligand has two functions: it first acts to fix the complex mechanically to the surface of the electrode and secondly acts as a molecular wire, i.e. funnels electrons into the Mo/W-N₂ system. However, since the bonding of nitrile has been found to become weak at an intermediate stage of N₂ reduction, the connection to the electrode established this way may become labile during the catalytic cycle and the complex may dissociate away from the surface. As a consequence, it appears to be necessary to additionally fix the Mo/W phosphine system to the surface (e.g. by linkers deriving from the phosphine ligands). Nevertheless, due to the weak covalency at intermediate stages of N_2 reduction the electron transfer properties of this group may also become poor during the catalytic cycle. As a consequence, it appears more promising to use a connection via the phosphine groups to the electrode to mediate electron transfer to complexes like **I**.

If Mo/W phosphine complexes with axial nitrile ligands are to be used for the homogeneous catalysis of N₂ reduction, it also has to be taken into account that the nitrile ligand is potentially labile during most of the catalytic cycle. In spite of this drawback, it may be meaningful to use this ligand in *trans* position to the N_2 group as it both stabilizes the Mo/W(0) oxidation state and activates the N2 group to the first (and most difficult) protonation step; this is not possible with ligands having π donor interactions [28]. As a consequence, the nitrile ligand has to be further attached to the metal phosphine complex in order to prevent (i) loss of this ligand during the catalytic cycle and/or (ii) exchange against a Lewis base deriving from the acid used for protonation. If this can be achieved synthetically, the trans position of the N2 group would effectively be blocked, i.e. protected from attack by an external ligand. This way, the unfavorable ligand exchange reactions at the trans position of N₂ could in fact be avoided.

7. Supplementary material

Tables of details of the structure determination, atomic coordinates, isotropic and anisotropic displacement parameters as well as bond lengths and angles for **I** are available upon request.

Acknowledgements

C.H. thanks U. Cornelissen for help with the spectroscopic measurements and N. Böres for help with preparative work. F.T. thanks the Fonds der Chemischen Industrie (FCI) for financial support.

References

- (a) F. Tuczek, N. Lehnert, Angew. Chem. 110 (1998) 2780;
 (b) R.L. Rawls, Chem. Eng. News 76 (1998) 29;
 (c) M. Fryzuk, S.A. Johnson, Coord. Chem. Rev. 200 (2000) 379;
 (d) D. Sellmann, J. Utz, N. Blum, F.W. Heinemann, Coord. Chem. Rev. 190–192 (0) (1999) 607;
 (e) R.L. Richards, Coord. Chem. Rev. 154 (1996) 83;
 (f) M. Hidai, Y. Mizobe, Chem. Rev. 95 (1995) 1115;
 (g) G.J. Leigh, Accts. Chem. Res. 25 (1992) 177.
- [2] (a) E.W. Triplett (Ed.), Prokaryotic Nitrogen Fixation: A Model System for the Analysis of a Biological Process, Horizon Scientific

- Press, Wymondham, UK, 2000;
- (b) B.K. Burgess, D.J. Lowe, Chem. Rev. 96 (1996) 2983;
- (c) J. Kim, D.C. Rees, Science 257 (1992) 1667;
- (d) J. Kim, D.C. Rees, Nature 360 (1992) 553;
- (e) M.K. Chan, J. Kim, D.C. Rees, Science 260 (1993) 792;
- (f) J. Chen, J. Christiansen, N. Campobasso, J.T. Bolin, R.C. Tittsworth, B.J. Hales, J.J. Rehr, S.P. Cramer, Angew. Chem. 105
- (1993) 1661; (a) LB Hawa
- (g) J.B. Howard, D.C. Rees, Chem. Rev. 96 (1996) 2965;
 (h) J.W. Peters, M.H.B. Stowell, S.M. Soltis, M.G. Finnegan, M.K. Johnson, D.C. Rees, Biochemistry 36 (1997) 1181;
 (i) J.T. Bolin, A.E. Ronco, T.V. Morgan, L.E. Mortenson, N.H. Xuong, Proc. Natl. Acad. Sci. USA 90 (1993) 1078.
- [3] (a) H. Deng, R. Hoffmann, Angew Chem. 105 (1993) 1125;
 (b) W. Plass, J. Mol. Struct., Theochem. 315 (1994) 53.
- [4] (a) M. Jimenez-Tenorio, M.C. Puerta, P. Valerga, D.L. Hughes, J. Chem. Soc., Dalton Trans. (1994) 2431;
 (b) T.A. George, B.B. Kaul, Q. Chen, J. Zubieta, Inorg. Chem. 32

(1993) 1706;

(c) T.A. George, L. Ma, S.N. Shailh, R.C. Tisdale, J. Zubieta, Inorg. Chem. 29 (1990) 4789;

(d) A. Galindo, A. Hills, D.L. Hughes, D.L. Richards, M. Hughes, J. Mason, J. Chem. Soc., Dalton Trans. (1990) 283;

(e) J.E. Barclay, A. Hills, D.L. Hughes, G.J. Leigh, C.J.

- Macdonald, M. Abu Bakar, H. Mohd-Ali, J. Chem. Soc., Dalton Trans. (1990) 2503;
- (f) M. Abu Bakar, D.L. Hughes, W. Hussain, G.J. Leigh, C.J. Macdonald, H. Mohd-Ali, J. Chem. Soc., Dalton Trans. (1988) 2545;
- (g) T.A. George, R.C. Tisdale, J. Am. Chem. Soc. 107 (1985) 5157;
- (h) J. Chatt, M.E. Fakley, P.B. Hitchcock, R.L. Richards, N.T. Luong-Thi, J. Chem. Soc., Dalton Trans. (1982) 345;

(i) T. Takahasi, Y. Mizobe, M. Sato, Y. Uchida, M. Hidai, J. Am. Chem. Soc. 102 (1980) 7461;

- (j) J. Chatt, A.J. Pearman, R.L. Richards, J. Chem. Soc., Dalton Trans. (1978) 1766;
- (k) J. Chatt, A.J. Pearman, R.L. Richards, J. Chem. Soc., Dalton Trans. (1977) 2139;
- (l) J. Chatt, A.J. Pearman, R.L. Richards, J. Chem. Soc., Dalton Trans. (1977) 1852;

(m) J. Chatt, A.J. Pearman, R.L. Richards, J. Chem. Soc., Dalton Trans. (1976) 1520;

(n) G.A. Heath, R. Mason, K.M. Thomas, J. Am. Chem. Soc. 96 (1974) 260;

(o) J. Chatt, G.A. Heath, R.L. Richards, J. Chem. Soc., Dalton Trans. (1974) 2074;

(p) J. Chatt, G.A. Heath, R.L. Richards, J. Chem. Soc., Chem. Commun. (1972) 1010.

- [5] R.N.F. Thorneley, D.J. Lowe, in: T.G. Spiro (Ed.), Molybdenum Enzymes, Wiley, New York, 1985.
- [6] R.A. Henderson, G.J. Leigh, C. Pickett, Adv. Inorg. Chem. Radiochem. 27 (1983) 197.
- [7] (a) N. Lehnert, B. Wiesler, F. Tuczek, A. Hennige, D. Sellmann, J. Am. Chem. Soc. 119 (1997) 8869;
 (b) N. Lehnert, B. Wiesler, F. Tuczek, A. Hennige, D. Sellmann, J. Am. Chem. Soc. 119 (1997) 8879;
 (c) E.B. Wiesler, N. Lehnert, F. Tuczek, J. Neuhausen, W. Tremel, Angew. Chem. 110 (1998) 856(Int. Ed. 37 815);
 (d) N. Lehnert, F. Tuczek, Inorg. Chem. 38 (1999) 1659;
 (e) N. Lehnert, F. Tuczek, Inorg. Chem. 38 (1999) 1671.
- [8] T. Tatsumi, M. Hidai, Y. Uchida, Inorg. Chem. 14 (1975) 2530.

- [9] J. Chatt, G.J. Leigh, H. Neukomm, C.J. Pickett, D.R. Stanley, J. Chem. Soc., Dalton Trans. (1980) 121.
- [10] S. Donovan-Mtunzi, R.L. Richards, J. Chem. Soc., Dalton Trans. (1984) 1329.
- [11] G.J. Leigh, C.J. Pickett, J. Chem. Soc., Dalton Trans. (1977) 1797.
- [12] J.R. Dilworth, R.L. Richards, Inorg. Synth. 20 (1980) 119.
- [13] G.M. Sheldrick, SHELXS-97 and SHELXS-97, in: Program for the Solution and Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1997.
- [14] J.A. Nelder, R. Mead, Comput. J. 7 (1965) 308.
- [15] T.H. Dunning, Jr., P.J. Hay, in: H.F. Schaefer, III (Ed.), Modern Theoretical Chemistry, Plenum Press, New York, 1976.
- [16] (a) P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 270 and 299;
 (b) W.R. Wadt, P.J. Hay, J. Chem. Phys. 82 (1985) 284.
- [17] (a) J.P. Foster, F. Weinhold, J. Am. Chem. Soc. 102 (1980) 7211;
 (b) A.B. Rives, F. Weinhold, Int. J. Quantum Chem. Symp. 14 (1980) 201;
 (c) A.E. Reed, R.B. Weinstock, F. Weinhold, J. Chem. Phys. 83

(1) A = B = 1 + A = C = C = E = W = 1 + 1 + C = D = 20 (1020)

(d) A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.

- [18] GAUSSIAN 98, Revision A.7, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian, Inc., Pittsburgh, PA, 1998.
- [19] G. Schaftenaar, MOLDEN version 3.2; CAOS/CAMM Center, University of Nijmegen, Nijmegen, The Netherlands.
- [20] A. Allouche, J. Pourcin, Spectrochim. Acta 49A (1993) 571.
- [21] C. Pelizzi, G. Pelizzi, Acta Crystallogr., Sect. B 35 (1979) 1785.
- [22] (a) T. Wagner, U. Englert, Struct. Chem. 8 (1997) 357;
 (b) C. Hue, W.C. Hodgeman, D.W. Benett, Inorg. Chem. 35 (1996) 1621.
- [23] M. Hidai, T. Kondama, M. Sato, M. Harakawa, Inorg. Chem. 15 (1976) 2694.
- [24] N.B. Colthup, L.H. Daly, S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, third ed., Academic Press, Orlando, FL, 1990.
- [25] (a) J.R. Dilworth, R.L. Richards, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 60 (and references therein), Pergamon Press, Oxford, 1982, p. 1073;

(b) J. Chatt, R.L. Richards, J. Organomet. Chem. 239 (1982) 65 (and references therein).

- [26] S. Donovan-Mtunzi, R.L. Richards, J. Chem. Soc., Dalton Trans. (1984) 469.
- [27] A.J. Lupinetti, S. Fau, G. Frenking, S.H. Strauss, J. Phys. Chem. A 101 (1997) 9558.
- [28] O. Franke, B.E. Wiesler, N. Lehnert, C. Näther, V. Ksenofontov, J. Neuhausen, F. Tuczek, Inorg. Chem. (2002), in press.
- [29] K.H. Horn, F. Tuczek, in preparation.
- [30] H.J.A. Jensen, P. Jørgensen, T. Helgaker, J. Am. Chem. Soc. 109 (1987) 2895.