Ligand-Based Reactivity

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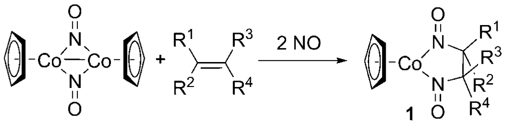
Synthesis of $[\text{RuCl}_2(\text{NO})_2(\text{THF})]$ and its Double C−N Bond-Forming Reactions with Alkenes**

Mark R. Crimmin, Robert G. Bergman, and F. Dean Toste**

While the activation of relatively inert gases such as N_2 and CO with organometallic complexes remains a topic of intense investigation, methods for controlling the reactivity of nitric oxide at transition-metal centers have received considerably less attention.[1–3] For example, the migratory insertion of NO into metal–alkyl or metal–aryl bonds has been observed in only a handful of metal complexes,[3] despite the analogous reaction of CO dominating its organometallic chemistry and being the key step in many homogeneous catalytic processes. Although the paucity of studies in this field may be a reflection of the often complicated background reactivity of NO,[4] the potential to develop selective reactions incorporating NO that form new carbon–nitrogen bonds represents an attractive approach in organic synthesis.

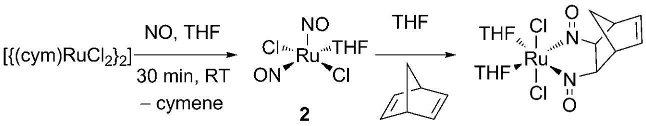
It is in this context that we are interested in the ligand-based reaction of metal nitrosyl complexes with alkenes.[5] In the absence of metal coordination the reaction chemistry of NO with alkenes is unruly.[4] Furthermore, only a few transition-metal complexes have been shown to promote this reaction selectively. Thus, inspired by an early finding of Brunner and Loskot, we demonstrated in the 1980s that $[\{\text{CpCo(NO)}\}_2]$, NO and strained or alkyl-substituted alkenes react cleanly to form the corresponding dinitrosoalkane complexes [**1**, Eq. (1)].[2,5a–c] More recently this chemistry has been used to develop a method for C−C bond formation.[5d,e] In addition, the reaction of $K[\text{IrCl}_5(\text{NO})]$ with alkenes to yield iridium nitrosoalkane complexes,[6] and the reaction of $[\text{TpRuCl}_2(\text{NO})]$ (Tp = tris(pyrazolyl)borate) with 2-vinylpyridine to yield a nitrosoalkene complex have been reported.[7]



(1)

In spite of the above reactions, there are not many C−N bond-forming reactions of metal nitrosyls and double additions remain especially rare. We now report an example of this type of reactivity with the novel dinitrosyl complex $[\text{RuCl}_2(\text{NO})_2(\text{THF})]$, which binds alkenes to the nitrosyl nitrogen atoms at room temperature in the presence of an additional neutral chelating ligand, L_2.

The reaction of $[\{(\text{cymene})\text{RuCl}_2\}_2]$ with 10 equiv of norbornadiene under an atmosphere of nitric oxide in $[D_8]$THF gave a putative six-coordinate ruthenium dinitrosoalkane adduct $[(\text{THF})_2\text{RuCl}_2\{(\mu\text{-NO})_2(C_7H_8)\}]$ in 86% yield as evidenced by ^{1}H NMR spectroscopy (Scheme 1).



Scheme 1. Reaction of $[\{(\text{cymene})\text{RuCl}_2\}_2]$ with NO and norbornadiene.

When the reaction was conducted without NO the alkene was not consumed. In addition, $[\text{Ru}_3(\text{CO})_{12}]$ proved an unsuitable starting material to access the same reaction product. Despite NMR data strongly suggesting alkene binding to the nitrosyl ligands of a ruthenium complex, the structure of the product could not be assigned by NMR spectroscopy alone. Attempts to isolate $[(\text{THF})_2\text{RuCl}_2\{(\mu\text{-NO})_2(C_7H_8)\}]$ were complicated by its instability in solution. These complexities were, however, resolved by isolating the metal dinitrosyl intermediate and studying its reaction chemistry (see below).

Performing the reaction of $[\{(\text{cymene})\text{RuCl}_2\}_2]$ with nitric oxide in THF in the absence of norbornadiene yielded $[\text{RuCl}_2(\text{NO})_2(\text{THF})]$ (**2**) as a brown crystalline solid in 88% yield (Scheme 1). In the solid state, **2** possesses near-perfect square-based pyramidal geometry at the metal ($\tau = 0.04$),[8] with one bent NO ligand occupying the apical site and one linear NO ligand occupying an equatorial site *trans* to coordinated THF (Figure 1). The remaining *trans*-disposed coordination sites of the basal plane are occupied by chloride ligands.

Complex **2** represents a rare example of a metal dinitrosyl complex possessing both linear and bent nitric oxide ligands in the solid state. The first structurally characterized example of such a complex, $[\text{RuCl(NO)}_2(\text{PPh}_3)_2]\text{PF}_6$ (**3**), was reported by Eisenberg and co-workers and, while cationic, provides an important point of comparison.[9,10] The bending of apical nitrosyl ligands in five-coordinate complexes has been the topic of theoretical discussions.[11] Although ruthenium–nitrogen bond lengths (**3**, 1.743(20) Å; **2**, 1.727(5) Å) and ruthe-

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[*] Dr. M. R. Crimmin, Prof. R. G. Bergman, Prof. F. D. Toste
Department of Chemistry, University of California
Berkeley, California, CA 94720 (USA)
E-mail: rbergman@berkeley.edu
fdtoste@berkeley.edu

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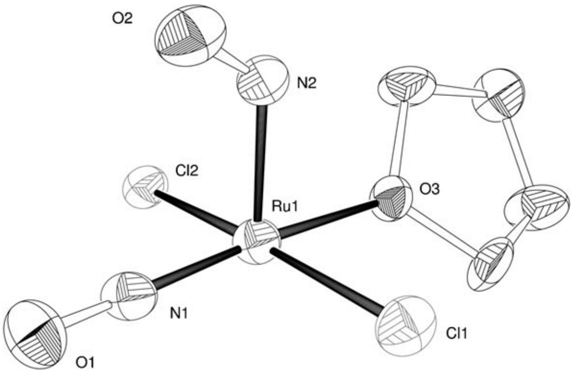
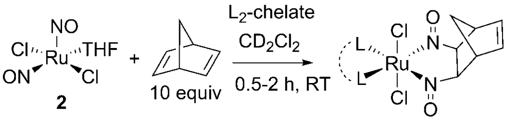


Figure 1. ORTEP representation of **2**; thermal ellipsoids at 50% probability. Selected bond angles [°] and lengths [Å]: Ru–N1 1.727(5), Ru–N2 1.915(5), Ru–O3 2.110(4), Ru–Cl1 2.349(2), Ru–Cl2 2.392(2), N1–O1 1.147(6), N2–O2 1.181(6); O1-N1-Ru 178.5(6), O2-N2-Ru 124.0(4).

nium–chlorine bond lengths (**3**, 2.362(6) Å; **2**, 2.349(2), 2.392(2) Å) within the basal plane of **2** are comparable to those reported for **3**, the apical ruthenium–nitrogen distance (**3**, 1.853(19) Å; **2**, 1.915(5) Å) in the latter cationic complex is noticeably shorter than that in **2**. While the charge difference between **2** and **3** may be responsible for this observation, a possible explanation for this effect may be found upon inspection of the unit cell of **2**. Coordination at ruthenium is augmented by a long-distance contact with a chloride ligand of an additional molecule within the asymmetric unit (see the Supporting Information, Figure S1). Residing *trans* to the apical NO ligand, the intermolecular ruthenium–chlorine bond of length 2.812(2) Å exceeds the sum of the van der Waals radii by some 0.3 Å, but this interaction may still be responsible for the lenthening of the apical Ru−NO bond by a *trans* effect.[12] Consistent with the single-crystal X-ray diffraction data, solid-state infrared data for **2** and **3** both show absorptions characteristic of linear (**2**, 1860 cm^{-1}; **3**, 1845 cm^{-1}) and bent (**2**, 1616 cm^{-1}; **3** 1687 cm^{-1}) NO coordination modes.

A series of NMR-scale reactions were conducted in CD_2Cl_2 solution between **2**, 10 equiv of norbornadiene and a series of κ^2-*N,N* and κ^2-*O,O* chelating L_2-type ligands. These reactions proceeded with displacement of THF from the coordination sphere of **2** to yield the corresponding six-coordinate dinitrosoalkane complexes [Eq. (2)]. The reaction has a broad ligand scope and tetramethylethylenediamine (TMEDA; 12%), 1,2-diaminobenzene (30%), (*R*)-(+)-1,1′-binaphthyl-2,2′-diamine (82%), 1,10-phenanthroline (30%), 2,2′-bipyridine (42%), 4,4′-di-*tert*-butyl-2,2′-bipyridine (54%), (*S,S*)-2,2′-methylenebis(4-*tert*-butyl-2-oxazoline) (20%), $[(2,4,6\text{-}Me_3C_6H_2)N{=}CH]_2$ (47%), and dimethoxyethane (78%) all promote alkene binding within 2 h at room temperature (in situ NMR yields in parentheses; the full details of these experiments are provided in the Supporting Information). In the absence of a coordinating ligand or in the presence of arylphosphine ligands no appreciable product formation was observed.



(2)

The tetramethylethylenediamine adduct [Eq. (2), $L_2 = Me_2NCH_2CH_2NMe_2$, **4a**] proved stable on the bench top and could be isolated and purified by chromatography on silica gel, without decomposition. ^1H and ^{13}C NMR data are consistent with the proposed formulation, infrared spectroscopic analysis reveals diagnostic NO stretches at 1396 and 1326 cm^{-1}, and electrospray ionization mass spectrometry displays the expected isotope pattern centered at 405.0626 *m/z* due to formation of $[M-Cl]^+$. As presented in Figure 2, in the solid state compound **4a** displays octahedral geometry at the ruthenium center. Ruthenium–nitrogen bonds to the dinitrosoalkane ligand (**4a**, 1.879(3), 1.883(3) Å) are drastically shorter than those to TMEDA (**4a**, 2.259(4), 2.266(3) Å) and shorter than those recorded for the six-coordinate ruthenium dioxime complex $[RuCl_2(PPh_3)_2\{(HON{=}CPh)_2\}]$ (Ru−N, 1.973(5), 1.962(6) Å),[13] consistent with significant metal back-donation into the π-system of the dinitrosoalkane ligand. Both nitrogen–oxygen (**4a**, 1.231(4), 1.227(4) Å; **1a**, 1.247(4), 1.252(4) Å) and nitrogen–carbon (**4a**, 1.508(3), 1.524(3) Å; **1a**, 1.492(5), 1.487(5) Å) bond lengths of the dinitrosoalkane moiety in **4a** are well reproduced when compared to the cobalt dinitrosoalkane complex of norbornene $[CpCo\{\mu\text{-}(NO)_2(C_7H_{10})\}]$ (**1a**).[2c]

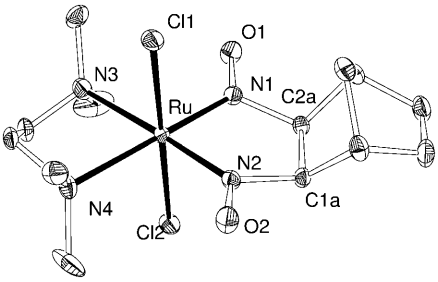
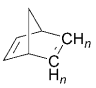
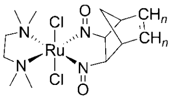
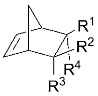
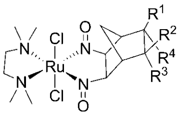
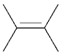
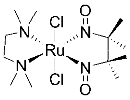
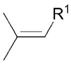
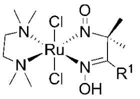
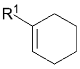
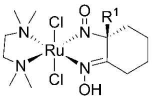
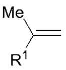
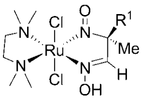


Figure 2. ORTEP representation of **4a**; thermal ellipsoids at 20% probability. Selected bond angles [°] and lengths [Å]: N1–Ru 1.879(3), N2–Ru 1.883(3), N3–Ru 2.259(4), N4-Ru 2.266(3), Cl1–Ru 2.3706(12), Cl2–Ru 2.3930(16), N1–O1 1.231(4), N2–O2 1.227(4), N1–C2A 1.508(3), N2-C1A 1.524(3), C1A–C2A 1.5448(4); N2-Ru-N1 84.33(14), N3-Ru-N4 81.32(14).

While the in situ NMR yield of **4a** derived from the reaction of **2** with TMEDA and norbornadiene in CD_2Cl_2 solution was only 12%, repeating this reaction in THF allowed the isolation of **4a** in 57% yield. THF is a coordinating solvent that could potentially promote alkene binding (see above). Two experiments conducted in $[D_8]$THF solution and monitored by ^1H NMR spectroscopy demonstrated that in this solvent multiple ligand-exchange reactions take place. The product of the reaction of TMEDA with **2** is unstable in solution and has yet to be characterized, while the product of reaction of TMEDA with $[(THF)_2RuCl_2\{(\mu\text{-}NO)_2\text{-}(C_7H_8)\}]$ is **4a**. As such, the origin of the increased reaction yield in THF compared to CD_2Cl_2 is currently not clear. Based upon these observations, the scope of alkene binding was investigated by conducting reactions of **2** with 10 equiv of TMEDA and 10–30 equiv of alkene in THF solution at room temperature (Table 1). Dinitrosoalkane adducts were only isolated from reactions with strained and non-enolizable alkenes (**4a–e**). For both 1,1-disubstituted and 1,1,2-trisubstituted alkenes, compounds containing a single nitrosoalkane and oxime functional group were isolated (**4 f–l**). Attempts to extend this methodology to both cyclic and acyclic, *cis-* and *trans*-1,2-dialkyl alkenes failed to yield products that were isolable by chromatography on silica gel.

Table 1: Scope of the reaction of **2**, 10 equiv of TMEDA and 10–30 equiv of alkene in THF at room temperature.

Alkene	Product			t [h]	Yield [%][a]
		$n=1$ $n=2$	**4a** **4b**	2 2	57 66
		$R^1=R^3=CO_2Me$ $R^2=R^4=H$ $R^3,R^4=\text{-(CH=CHCH}_2\text{)-}$ $R^1=R^2=H$	**4c** **4d**	0.5 2	60 75
			**4e**	2	81[b]
		$R^1=Me$ $R^1=iPr$	**4f** **4g**	0.5 3	93[b] 24[b]
		$R^1=Me$ $R^1=Ph$	**4h** **4i**	0.5 2	66[b] 56[b]
		$R^1=Ph$ $R^1=CH_2(tBu)$ $R^1=iPr$	**4j** **4k** **4l**	1 0.5 0.5	81[b] 88[b] 44[b]

[a] Reactions conducted in THF at room temperature using 10 equiv of TMEDA, 1 equiv of **2**, and 10 equiv of alkene; reported yields are following isolation by silica gel chromatography. [b] 30 equiv of alkene was used.

Tautomerization was detected by not only the acidic oxime proton signal, observed as a broad resonance between $\delta=6.0$–6.6 ppm and $\delta=7.6$–9.2 ppm for **4 f–i** and **4j–l**, respectively, in $CDCl_3$ solution by ^{1}H NMR spectroscopy, but also distinctive resonances at $\delta=155$–175 ppm in the ^{13}C NMR spectra characteristic of the sp^2-oxime carbon. In addition, broad ν(O−H) absorptions were observed in the infrared spectra between 3100–3250 cm^{-1}. The connectivity of **4l** was determined unambiguously following a single-crystal X-ray diffraction experiment; however, the poor resolution of the data limits any informative discussion (see the Supporting Information, Figure S2). It is noteworthy that while analogous tautomerization products have not been observed in the alkene/[CpCo(NO)$_2$] reaction,[2] a similar tautomerization has been observed in the insertion reaction of [NO][PF$_6$] with [CpCr(NO)$_2$Me] to yield [CpCr(NO)$_2${N(OH)CH$_2$}][PF$_6$],[14] and upon reaction of [{(η^3-allyl)NiBr}$_2$] with NO to form [NiBr(NO)(CH$_2$=CH−CH=NOH)].[3a]

In summary, a simple high-yielding synthesis of the novel metal dinitrosyl complex [RuCl$_2$(NO)$_2$(THF)] from [{(cymene)RuCl$_2$}$_2$] is reported. In the solid state, the former compound displays nitric oxide ligands with both bent and linear geometries. In solution, in the presence of a variety of chelating ligands, [RuCl$_2$(NO)$_2$(THF)] reacts with simple alkenes to form the corresponding six-coordinate dinitrosoalkane complexes. We are continuing to investigate new organometallic reagents for controlling the reactivity of NO and the application of the reaction reported herein to the asymmetric diamination of alkenes and will report our findings in subsequent publications.

Experimental Section

Synthesis of **2**: A Schlenk flask containing a slurry of [{RuCl$_2$(cymene)}$_2$] (2.00 g, 3.26 mmol) in THF (50 mL) was attached to a manifold fitted with a nitric oxide inlet. The reaction mixture was freeze–pump–thaw degassed and the apparatus isolated under vacuum. Nitric oxide was then introduced and the reaction mixture stirred under 1 atm NO. A fast reaction occurred and the solution turned deep brown with solid [{RuCl$_2$(cymene)}$_2$] being consumed in the first 30 min. Once the reaction was complete, the solvent was removed in vacuo and the resulting brown/black crystalline solid washed with pentane (3 × 20 mL) and dried under vacuum overnight. [RuCl$_2$(NO)$_2$THF] (1.74 g, 5.72 mmol, 88 %) was isolated as a brown solid. ^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K): $\delta=4.60$ (m, 4H, THF), 2.20 ppm (m, 4H, THF); ^{13}C NMR (CD_2Cl_2, 100 MHz, 298 K): $\delta=75.5$, 26.7 ppm; IR (solid): $\tilde{\nu}=1859$, 1615 cm^{-1}; Elemental analysis calcd for $C_4H_8N_2O_3RuCl_2$: C 15.80, H 2.65, N 9.21; found: C 16.23, H 2.48, N 8.54.

Synthesis of **4a**: In a glovebox, TMEDA (190 mg, 1.64 mmol, 10 equiv) and norbornadiene (151 mg, 1.64 mmol, 10 equiv) were weighed into a scintillation vial and dissolved in THF (2.5 mL). This mixture was then added to a solution of **2** (50 mg, 0.164 mmol) in THF (2.5 mL) in a 20 mL scintillation vial. The reaction mixture was stirred for 2 h at room temperature. The vial containing the reaction mixture was removed from the glovebox and the crude mixture chromatographed on silica gel using chloroform as an eluent. **4a** was isolated as a red/brown crystalline solid (40.7 mg, 0.0927 mmol, 57 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): $\delta=1.52$ (d, 1H, $J=9.6$ Hz), 1.63 (d, 1H, $J=9.6$ Hz), 2.39–2.46 (m, 2H), 2.50–2.56 (m, 2H), 2.61 (s, 6H), 2.90 (s, 6H), 3.57 (m, 2H), 4.01 (m, 2H), 6.37 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): $\delta=45.3$, 49.3, 50.5, 51.2, 59.7, 100.3, 140.1 ppm; IR (solid): $\tilde{\nu}=2910$, 1460, 1397, 1326, 1270 cm^{-1}; HR-MS (ESI, $[M-Cl]^+$) calcd for $C_{13}H_{24}ClN_4O_2Ru$ 405.0631, found 405.0626. Elemental analysis calcd for $C_{13}H_{24}Cl_2N_4O_2Ru$: C 35.46, H 5.49, N 12.72; found: C 35.23, H 5.55, N 12.60.

Full experimental details including single-crystal X-ray diffraction studies are provided in the Supporting Information. CCDC 810236 (**2**) and 810237 (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] a) G. B. Richter-Addo, P. Legzdins, *Metal Nitrosyls*, Oxford University Press, New York, **1992**; b) G. B. Richter-Addo, P. Legzdins, *Chem. Rev.* **1988**, *88*, 991; c) T. W. Hayton, P. Legzdins, W. B. Sharp, *Chem. Rev.* **2002**, *102*, 935; d) K. K. Pandey, *Coord. Chem. Rev.* **1983**, *51*, 69.

[2] a) H. Brunner, S. Loskot, *Angew. Chem.* **1971**, *83*, 546; *Angew. Chem. Int. Ed. Engl.* **1971**, *10*, 515; b) H. Brunner, S. Loskot, *J. Organomet. Chem.* **1973**, *61*, 401; c) G. Evrard, R. Thomas, B. R. Davis, I. Bernal, *J. Organomet. Chem.* **1977**, *124*, 59.

[3] a) R. A. Clement, U. Klabunde, G. Parshall, *J. Mol. Catal.* **1978**, *4*, 87; b) W. P. Weiner, M. A. White, R. G. Bergman, *J. Am. Chem. Soc.* **1981**, *103*, 3612; c) W. P. Weiner, R. G. Bergman, *J. Am. Chem. Soc.* **1983**, *105*, 3922; d) M. D. Seidler, R. G. Bergman, *J. Am. Chem. Soc.* **1984**, *106*, 6110; e) M. D. Seidler, R. G. Bergman, *J. Am. Chem. Soc.* **1983**, *105*, 1897; f) A. Goldhaber, K. P. C. Volhardt, E. C. Walborsky, M. Wolfgruber, *J. Am. Chem. Soc.* **1986**, *108*, 516; g) M. W. Schoonover, E. C. Baker, R. Eisenberg, *J. Am. Chem. Soc.* **1979**, *101*, 1880; h) P. C. Wailes, H. Weigold, A. P. Bell, *J. Organomet. Chem.* **1972**, *34*, 155; i) A. R. Middleton, G. Wilkinson, *J. Chem. Soc. Dalton Trans.* **1980**, 1888.

[4] Reactions of NO with alkenes are reported to occur only in the presence of trace NO_2 impurities and, due to the instability of radical intermediates, often yield a complex mixture of products. For example, 1,2-dimethylbut-2-ene reacts with NO at 24 °C and 50 psi to form a mixture containing more than ten compounds. See a) J. F. Brown, Jr., *J. Am. Chem. Soc.* **1957**, *79*, 2480; b) C. A. Burkhard, J. F. Brown, Jr., *J. Org. Chem.* **1964**, *29*, 2235; c) L. V. Phillips, D. M. Coyne, *J. Org. Chem.* **1964**, *29*, 1937; d) K. W. Chiu, P. D. Savage, G. Wilkinson, D. J. Williams, *Polyhedron* **1985**, *4*, 1941; e) A. Rockenbauer, M. Gyor, F. Tudos, *Tetrahedron Lett.* **1986**, *27*, 3425; f) J. S. B. Park, J. C. Walton, *J. Chem. Soc. Perkin Trans. 2* **1997**, 2579.

[5] a) P. N. Becker, M. A. White, R. G. Bergman, *J. Am. Chem. Soc.* **1980**, *102*, 5676; b) P. N. Becker, R. G. Bergman, *Organometallics* **1983**, *2*, 787; c) P. N. Becker, R. G. Bergman, *J. Am. Chem. Soc.* **1983**, *105*, 2985; d) J. M. Schomaker, W. C. Boyd, I. C. Stewart, F. D. Toste, R. G. Bergman, *J. Am. Chem. Soc.* **2008**, *130*, 3777; e) W. C. Boyd, M. R. Crimmin, L. E. Rosebrugh, J. M. Schomaker, R. G. Bergman, F. D. Toste, *J. Am. Chem. Soc.* **2010**, *132*, 16365.

[6] N. Escola, D. A. Llberia, G. Leitus, F. Doctorovich, *Organometallics* **2006**, *25*, 3799.

[7] Y. Arikawa, T. Asayama, K. Itatani, M. Onishi, *J. Am. Chem. Soc.* **2008**, *130*, 10508.

[8] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc. Dalton Trans.* **1984**, 1349.

[9] a) C. G. Pierpont, R. Eisenberg, *Inorg. Chem.* **1972**, *11*, 1088; b) C. G. Pierpont, D. G. Van Derveer, W. Durland, R. Eisenberg, *J. Am. Chem. Soc.* **1970**, *92*, 4760.

[10] a) J. P. Collman, P. Farnham, G. Dolcetti, *J. Am. Chem. Soc.* **1971**, *93*, 1788; b) L. K. Bell, J. Mason, D. M. P. Mingos, D. G. Tewt, *Inorg. Chem.* **1983**, *22*, 3497; c) J. Mason, D. M. P. Mingos, J. Schaefer, D. Sherman, E. O. Stejskalc, *J. Chem. Soc. Chem. Commun.* **1985**, 444; d) J. Mason, D. M. P. Mingos, D. Sherman, R. W. M. Wardleb, *J. Chem. Soc. Chem. Commun.* **1984**, 1223.

[11] a) R. Hoffmann, M. M. L. Chen, M. Elian, A. R. Rossi, D. M. P. Mingos, *Inorg. Chem.* **1974**, *13*, 2666; b) R. Hoffmann, M. M. L. Chen, D. L. Thorn, *Inorg. Chem.* **1977**, *16*, 503; c) R. Eisenberg, C. D. Meyer, *Acc. Chem. Res.* **1975**, *8*, 26.

[12] B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Echeverria, E. Cremades, F. Barragan, S. Alvarez, *Dalton Trans.* **2008**, 2832.

[13] A. K. Das, S.-M. Peng, S. Bhattacharya, *Polyhedron* **2001**, *20*, 327.

[14] a) P. Legzdins, A. C. Willis, *J. Am. Chem. Soc.* **1986**, *108*, 317; b) P. Legzdins, G. B. Richter-Addo, B. Wassink, F. W. B. Einstein, R. H. Jones, A. C. Wills, *J. Am. Chem. Soc.* **1989**, *111*, 2097.