may become significant for industrial production of those novel materials.[3] As demonstrated above, the procedure and the chemicals used for the synthesis of high-quality CdS nanocrystals are simple, safe, and inexpensive in comparison to those reported previously.[8,15,16]

Experimental Section

Typically, a mixture (4 g in total) of CdO (0.0128 g, 0.10 mmol), oleic acid (0.30 – 21.2 mmol), and technological-grade ODE (Aldrich) was heated to 300 °C. A solution of sulfur (0.0016 g, 0.05 mmol) in ODE was swiftly injected into this hot solution, and the reaction mixture was allowed to cool to 250 °C for the growth of CdS nanocrystals. The synthesis can be carried out under argon or open to air. Aliquots were taken at different time intervals, and UV/Vis and PL spectra were recorded for each aliquot. XRD and TEM measurements were also performed to characterize the crystallinity, size, and size distribution of the resulting crystals. The size-distribution diagrams were obtained by measuring about 500 individual CdS nanocrystalline particles on enlarged photographs. All the measurements were performed on the original aliquots without any size sorting. The unconsumed cadmium precursor was separated from the nanocrystals by the repeated extraction of the reaction aliquots with an equal volume of $CHCl_3/CH_3OH$ (1:1). The extraction process was monitored by a UV/Vis absorption spectrophotometer. The size of the resulting nanocrystals were determined by TEM measurements and literature data on size versus the position of the first sorption peak.[8,16] The characterization and sample preparation of the nanocrystals, including X-ray diffraction, TEM, PL, and UV/Vis, were reported in a previous paper.[14] The size distribution was also determined by using the method reported in ref. [14] The CdSe and ZnSe nanocrystals were synthesized in a similar fashion; the selenium precursor was a solution of selenium/tributylphosphane (1:1.1) in ODE.

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An Umpolung Approach to *cis*-Hyponitrite Complexes**

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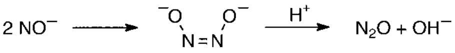
Dedicated to Professor Karl Wieghardt
on the Occasion of his 60th Birthday

The reductive dimerization of nitric oxide to give nitrous oxide is an important process both in the remediation of nitrogen-oxide pollutants in flue and exhaust gases by heterogeneous platinum metals,[1] and in the use of the oxyanions of nitrogen as terminal electron acceptors by dissimilatory bacteria.[2] In these transformations the key step is the formation of the nitrogen – nitrogen double bond, and here the frequently proposed mechanism is the stereospecific dimerization of nitroxyl, NO^-, to give *cis* hyponitrite, followed by elimination of nitrous oxide, [Eq. (1)].[3]



$$2\,NO^- \longrightarrow {}^-O\text{–}N{=}N\text{–}O^- \xrightarrow{H^+} N_2O + OH^- \qquad (1)$$

Unlike *trans* hyponitrite, for which there is an extensive and well established structural,[4] mechanistic,[5–8] and derivative chemistry,[9] our knowledge of *cis* hyponitrite is sparse. Although an elegant spectroscopic and structural study of sodium *cis* hyponitrite,[10,11] derived from the solid-state reaction of sodium oxide and nitrous oxide, established a new benchmark for this area, the reactivity of the free or coordinated dianion remains vaguely outlined. Thus key aspects of the kinetics and mechanism of the decomposition of *cis* hyponitrite, its coordination chemistry, and alkylation remain unknown. Furthermore, there is only a solitary structurally characterized complex of a chelated mononuclear *cis* hyponitrite, $[Pt(\eta^2\text{-}O_2N_2)(PPh_3)_2]$, which results from the equally unique oxidative coupling of two nitric oxides by $[Pt(PPh_3)_4]$.[12–18] Related reactions for different late transition metals are thought to give *trans*-hyponitrite complexes.[19–21] Herein we describe: 1) a new general method for the introduction and stabilization of *cis* hyponitrite in the coordination sphere of a metal, 2) the structure of one of these complexes, $[Ni(\eta^2\text{-}O_2N_2)(dppf)]$, (dppf = 1,1′-bis(diphenylphosphanyl)ferrocene), and 3) the reactivity of these new *cis*-hyponitrite complexes.

We recently described the synthesis of a new class of diazeniumdiolates, $RN_2O_2^-$, from the base-mediated condensation of 2,4,6-trisubstituted phenols with nitric oxide.[22] In the course of characterizing one of these derivatives, with R = OMe, **1**, we observed rapid acid-promoted stoichiometric

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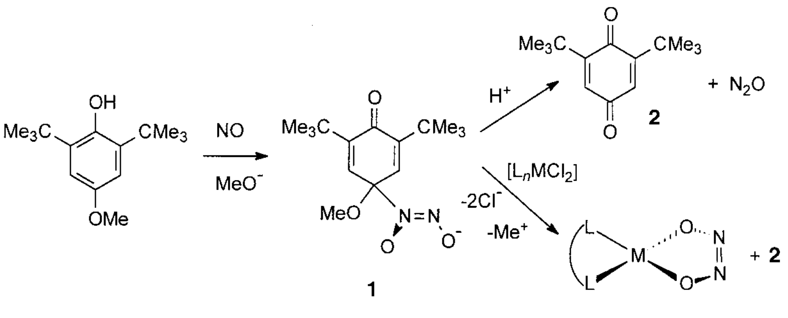

	a	b	c	d	e	f
M	Ni	Ni	Pt	Pt	Pt	Pt
L_n	dppf	diphos	dppf	diphos	$PMePh_2$	PPh_3

Scheme 1.

decomposition to generate nitrous oxide and 2,6-di-*tert*-butylbenzoquinone (**2**; Scheme 1). This unusual umpolung in the heterolysis of the C–N bond suggested that the reaction might occur for other electrophiles, most notably transition metals. In this case the result proves to be a new approach to *cis*-hyponitrite complexes. Thus the reaction of **1** and divalent Group 10 transition-metal complexes results in the rapid formation of new diamagnetic square-planar *cis*-hyponitrite complexes, **3a–e**, at room temperature in high yield, as well as known *cis*-hyponitrite complex **3f** (Scheme 1, diphos = 1,2-ethanediyldis[(diphenyl)phosphane]). The net transfer of $N_2O_2^{2-}$ to a transition metal from a diazeniumdiolate such as **1** is a new reactivity pattern for these reagents which usually form chelates or occasionally reductively nitrosylate metal centers.[23] Crystallographic characterization of **3a** by single-crystal X-ray diffraction (Figure 1) confirms the chelation of a *cis*-hyponitrite ligand in a square-planar complex. The dppf ligand adopts a common[24] but compact synclinal staggered configuration with the P(1)-centroid(1)-centroid(2)-P(2) dihedral angle (τ) of 28.5°. Prior structural determinations of *cis*-hyponitrite complexes, $[(H_3N)_5CoN(O)NOCo(NH_3)_5](NO_3)_4$,[25] and $[Pt(\eta^2\text{-}O_2N_2)(PPh_3)_2]$,[12] have proven troublesome and were only refined to conventional *R* factors of 16 and 11%, respectively, for the more intense data.

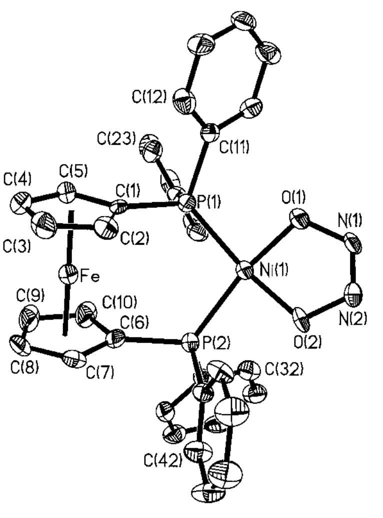

Figure 1. ORTEP representation for **3a** with the hydrogen atoms omitted. Selected bond lengths [Å] and angles [°]: Ni(1)-O(1) 1.820(4), Ni(1)-O(2) 1.818(4), O(1)-N(1) 1.400(6), N(1)-N(2) 1.236(6), N(2)-O(2) 1.385(5), Ni(1)-P(1) 2.180(2), Ni(1)-P(2) 2.205(2); O(1)-Ni(1)-O(2) 83.9(2), Ni(1)-O(1)-N(1) 112.2(3), O(1)-N(1)-N(2) 115.4(4), N(1)-N(2)-O(2) 115.4(5), N(2)-O(2)-Ni(1) 112.9(3), P(1)-Ni(1)-P(2) 101.59(6).

Unlike *trans* hyponitrite which is readily protonated or alkylated to give metastable RONNOR or $RONNO^-$ adducts ($R = H^+$ or R^+),[9] the only known metastable derivatives of *cis* hyponitrite involve O,O chelation or O,N dicoordination to transition-metal centers. Thus *cis* RONNOR or *cis* $RONNO^-$ are unknown, and the latter have been theoretically predicted to have very low energy barriers for the elimination of RO^- ions and nitrous oxide.[9] Electrophiles, such as HCl or Me_3SiCl, readily cleave **3a–f** to return $[L_2MCl_2]$ and nitrous oxide. Nitrous oxide is also generated during the thermolysis of **3a–f**, which all exothermally decompose at relatively low temperatures, between 75 and 120 °C, to give black insoluble residues. In addition to their thermal instability the new *cis*-hyponitrite complexes **3a–e** photolytically decompose upon UV irradiation.

To spectrophotometerically follow the kinetics of their thermal decomposition reactions we have incorporated the chelating phosphane ligand dppf in **3a,c**, to act as a visible chromophore. When the ferrocene-based absorption, $\lambda_{max} = 406$ nm for **3a**, is used to monitor their thermal decomposition in DMF at 40 °C the kinetics are first order in complex alone, with $k = 3.3 \pm 0.2 \times 10^{-4}\,s^{-1}$, and are independent of the initial complex concentration and of added triphenylphosphane, even when the $[PPh_3]$ is three orders-of-magnitude higher than [**3a**]. Although there is little solvent effect on the rate of **3a** decomposition, for example, in dimethylacetamide under the above conditions, the decomposition again follows triphenylphosphane-independent first-order kinetics with $k = 3.8 \pm 0.3 \times 10^{-4}\,s^{-1}$. In dichloromethane black insoluble products interfere with the kinetic measurements. Moreover, nitrous oxide release into the gas phase, monitored by the IR absorbance of the $\nu(N_2O)$ band at 2224 cm^{-1}, also follows the same kinetic profile with $k = 1.5 \pm 1.1 \times 10^{-4}\,s^{-1}$ for the decomposition of **3a** in DMF at 40 °C. Taken together, the kinetics results indicate that the rate-limiting step in the decomposition of **3a** is unimolecular and accompanies release of nitrous oxide. The resulting reactive fragment, formally a terminal oxo complex [(dppf)NiO], which results from loss of nitrous oxide, is similar to some of the intermediates which have been proposed for carbon dioxide exchange in $[Pt(\eta^2\text{-}O_2CO)(PPh_3)_2]$.[26] In support of the presence of such a proposed reactive intermediate in the decomposition of **3f** we have treated dichloromethane solutions of **3f** at reflux with saturating pressures of carbon dioxide or excess carbon disulfide and find that among the platinum-containing products are $[Pt(\eta^2\text{-}O_2CO)(PPh_3)_2]$, and $[Pt(\eta^2\text{-}S_2CO)(PPh_3)_2]$, respectively, in addition to $[PtCl_2(PPh_3)_2]$.

In summary, a new general method to prepare *cis*-hyponitrite complexes from the diazeniumdiolate compound **1** is described and a high-resolution structure of one such derivative has been determined. The decomposition of these complexes suggests rate-limiting loss of nitrous oxide leads to unusual and reactive late-transition-metal terminal oxo intermediates.

Experimental Section

3a: [Ni(dppf)Cl$_2$],[27] (268 mg) dissolved in CH$_2$Cl$_2$ (15 mL) was treated in one addition with **1**[22] (2 equivalents, 249 mg) suspended in methanol (60 mL). Rapidly a deep orange color developed and the solution volume was immediately reduced to ca 10 mL by evaporation at ambient temperatures. The resulting bright orange crystals were isolated by filtration and washed with portions of cold methanol (4 × 10 mL) or until the filtrate was colorless. Recrystallization of this product from dichloromethane/ethanol at room temperature returns 243 mg (93 % yield) of **3a**. Elemental analysis calcd (%) $C_{34}H_{28}FeN_2NiO_2P_2 \cdot \frac{1}{2}CH_2Cl_2$: C 59.26, H 4.05, N 3.88; found: C 59.43, H 4.28, N 3.64; IR (KBr,): $\tilde{\nu} = 1480$ m, 1449 s, 1436 s, 1307 m, 1194 w, 1182 w, 1168 m, 1096 s, 1036 m, 1028 m, 999 w, 983 m, 917 m, 827 w, 799 m, 744.3 s, 692 s, 638 w, 625 m, 556 m, 510, s, 494 s, 471 cm^{-1} m; ^{1}H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 7.84$ (m, 8H), 7.52 (m, 4H), 7.42 (t, $J = 7.3$ Hz, 8H), 4.42 (m, 4H), 4.26 ppm (m, 4H); ^{3}P NMR (162 MHz, CD$_2$Cl$_2$): $\delta = 25.0$ ppm (s) (UV/Vis: λ_{max}, (ε_{max}, M^{-1}cm^{-1}) in CH$_2$Cl$_2$: 406 nm (655); differential scanning calorimetry (DSC): $\Delta H = -802$ kcal mol^{-1} $T_{onset} = 75$ °C. Crystals suitable for X-ray diffraction were grown from CH$_2$Cl$_2$/Et$_2$O at −15 °C.

Crystal data for **3a**: $C_{35}H_{28}Cl_2FeN_2NiP_2O_2$, $M = 755.99$, 143 K, triclinic space group $P\bar{1}$, $a = 10.6210(8)$, $b = 11.3831(9)$, $c = 15.515(2)$ Å, $\alpha = 84.021(2)$, $\beta = 72.745(2)$, $\gamma = 69.790(1)°$, $V = 1681.0(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.494$ Mg m^{-3}, $F(000) = 772$, 426 parameters; R_1 (wR_2) [$I > 2\sigma(I)$] = 0.064 (0.15), s(GOF) = 0.98. Crystals of **3a** were mounted on glass fibers with epoxy resin and diffraction data was collected on a Bruker Smart CCD diffractometer equipped with a sealed molybdenum tube which was monochromated to give $\lambda = 0.71073$ Å. The structure was solved using direct methods and refined using full-matrix least-squares on F^2 with SHELXTL. With the exception of the disordered dichloromethane solvate, all non-hydrogen atoms were refined anisotropically with element assignments as described in the text. CCDC-176081 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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Aminocyclopentadienyl Ruthenium Chloride: Catalytic Racemization and Dynamic Kinetic Resolution of Alcohols at Ambient Temperature[**]

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Dynamic kinetic resolution (DKR) is an attractive method for the complete transformation of a racemic mixture into a single enantiomer.[1] The DKR of secondary alcohols is a prominent example, for which transition-metal-catalyzed racemization is coupled with enzymatic acylation.[2] In particular, Bäckvall and co-workers have introduced a notable catalyst system that provides a wide range of chiral acetates in good yields and excellent optical purities.[2b–f] However, the catalyst for the racemization of secondary alcohols is activated at high temperature, and needs the corresponding ketones as hydrogen mediators.[3] Thus, the catalyst system requires a thermally stable lipase; *p*-chlorophenyl acetate has been selected as an acyl donor,[2c] because oxidation of the starting alcohols occurs when the conventional alkenyl acetates are used as acyl donors.[4]

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