ORGANOMETALLICS

Volume 23, Number 24, November 22, 2004

Communications

Synthesis and Reactivity of a Mononuclear Parent Amido Nickel Complex. Structures of $Ni[C_6H_3\text{-}2,6\text{-}(CH_2P^iPr_2)_2](NH_2)$ and $Ni[C_6H_3\text{-}2,6\text{-}(CH_2P^iPr_2)_2](OMe)$

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Received September 4, 2004

Summary: The first example of a nickel parent amido complex, Ni(PCP)(NH_2), has been synthesized and structurally characterized. This compound reacts quantitatively with water and methanol to give the mononuclear hydroxide and methoxide derivatives Ni(PCP)(OH) and Ni(PCP)(OMe). Ni(PCP)(NH_2) behaves as a strong nucleophile and adds rapidly to benzaldehyde, affording an equimolecular mixture of the aldimido derivative Ni(PCP)(N=CHPh), the hydroxide Ni(PCP)(OH), and ammonia.

The synthesis and reactivity of late-transition-metal complexes possessing amido (NR_2^-) and alkoxide (OR^-) ligands have received considerable attention in recent years.[1] These complexes have been proposed as intermediates in a number of catalytic processes.[2] Despite these efforts, examples of the parent amides, M−NH_2, continue to be scarce.[3−5] This is possibly due to the difficulty that the high reactivity of late-transition-metal amides, usually interpreted as a result of the combination of a "soft" late transition metal with a "hard" donor ligand,[6] poses to their synthesis and isolation, especially in the case of the parent species. Furthermore, amido and alkoxo complexes display a pronounced tendency to associate, forming binuclear or polynuclear species.[7] It has not been until recently that some parent amido complexes of middle and late transition metals, such as iridium[4] and iron and ruthenium,[5] have been reported. Similarly, alkoxo complexes of the late transition elements remain uncommon. In this communication we report the synthesis, structural characterization, and

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[1] See for instance: Fulton, J. R.; Holland, A. W.; Fox, D. J.; Bergman, R. G. *Acc. Chem. Res.* **2002**, *35*, 44 and references herein.

[2] (a) Cornils, B.; Herrmann, W. A. *Applied Homogeneous Catalysis with Organometallic Compounds*; VCH: New York, 1996; Vol. 1. (b) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999. (c) Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163. (d) Roundhill, D. M. *Chem. Rev*. **1992**, *92*, 11.

[3] (a) Dewey, M. A.; Knight, D. A.; Gladysz, J. A. *Chem. Ber,* **1992**, *125*, 815. (b) Joslin, F. L.; Jonson, M. P.; Mague, J. T.; Roundhill, D. M. *Organometallics* **1991**, *10*, 41. (c) Tahmassebi, S. K.; McNeil, W. S.; Mayer, J. M. *Organometallics* **1997**, *16*, 5342. (d) Jayaprakash, K. N.; Conner, D.; Gunnoe, T. B. *Organometallics* **2001**, *20*, 5254.

[4] Kanzelberger, M.; Zhang, X.; Emge, T. J.; Goldman, A. S.; Zhao, J.; Incarvito, C.; Hartwig, J. F. *J. Am. Chem. Soc*. **2003**, *125*, 13644.

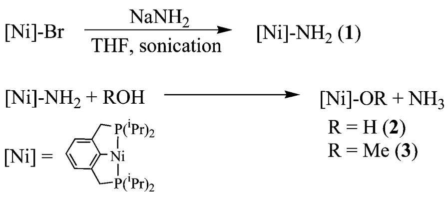
[5] (a) Fulton, J. R.; Bouwkamp, M. W.; Bergman, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 8799. (b) Fulton, J. R.; Sklenak, S.; Boukamp, M.; Bergman, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 4722. (c) Holland, A. W.; Bergman, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 14684. (d) Kaplan, A. W.; Ritter, J. C. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1998**, *120*, 6828. (e) Fox, D. J.; Bergman, R. G. *J. Am. Chem. Soc.* **2003**, *125*, 8984. (f) Fox, D. J.; Bergman, R. G. *Organometallics* **2002**, *23*, 1656.

[6] For a recent discussion see for instance: Holland, P. L.; Andersen, R. A.; Bergman, R. G. *Comments Inorg. Chem*. **1999**, *21*, 115.

[7] A search in the CCDC database (version 5.27, Nov 2003) afforded 67 structures of metal complexes containing μ-NH_2 ligands.

10.1021/om049312r CCC: $27.50 © 2004 American Chemical Society
Publication on Web 10/27/2004

Scheme 1



some reactivity studies of a mononuclear Ni complex that features a terminally bonded amido unit, Ni−NH$_2$. In addition, we report the crystal structure of a mononuclear methoxide derivative. Dimerization of these complexes has been prevented by the use of the tridentate pincer ligand 2,6-bis((diisopropylphosphino)methyl)phenyl (PCP). The two complexes reported herein constitute very unusual examples in the chemistry of group 10 metals. To our knowledge, no structural data for mononuclear group 10 M−NH$_2$ complexes have been hitherto reported.

We have recently shown that sonication of a suspension of the precursors M(PCP)X (M = Ni, X = Br; M = Pd, X = NO$_3$) and NaOH in THF leads to the mononuclear nickel and palladium hydroxides M(PCP)(OH).[8] Use of NaNH$_2$ in place of the hydroxide reagent allows the preparation of the Ni amido complex Ni(PCP)(NH$_2$) (**1**)[9] as an orange crystalline solid in 70% isolated yield (Scheme 1). For M = Pd, a new complex is formed (detected as a singlet resonance at δ 59.0 ppm by ^{31}P{^{1}H} NMR spectroscopy), but its high reactivity has hitherto prevented its isolation.

Complex **1** is very soluble in common organic solvents. Its ^{31}P{^{1}H} NMR spectrum displays a singlet at δ 60.8 ppm, whereas in the ^{1}H NMR spectrum, a slightly broad triplet at δ −1.00 ppm ($^3J_{HP}$ = 8.3 Hz) can be assigned to the NH$_2$ protons. IR absorptions associated with ν_{as} and ν_s NH$_2$ stretching modes are observed at 3355 and 3295 cm^{-1}, respectively.

The structural assignment of the amido complex **1** has been confirmed by X-ray crystallography.[10] Crystals suitable for an X-ray diffraction study were obtained from a concentrated hexamethyldisiloxane solution at room temperature. Two crystallographically independent molecules displaying similar bond distances and angles form the asymmetric unit of complex **1**. At variance with the analogous hydroxide Ni(PCP)(OH) (**2**),[8] no intermolecular contacts can be found in the solid state. Figure 1 shows an ORTEP perspective of one such molecule. The Ni−N bond in complex **1** (average 1.872(2) Å), while slightly shorter than in Ni(2,4,6-Me$_3$C$_6$H$_2$)(NHPh)(PMe$_3$)$_2$[11] (1.931(3) Å), is appreciably longer than the formally double Ni=N bond length of 1.702(2) Å reported by Hillhouse et al. for the three-coordinate nickel−imido complex Ni(=NC$_6$H$_3$-2,5-iPr$_2$)(dtbpe).[12] Even though the amido hydrogen atoms were located in positions that suggest a planar configuration of the NH$_2$ group, this is probably the result of the averaging of two equally populated orientations of the pyramidal NH$_2$ fragment.[5e] DFT calculations on models of Ni(PCP)(NH$_2$) support this assumption.[13]

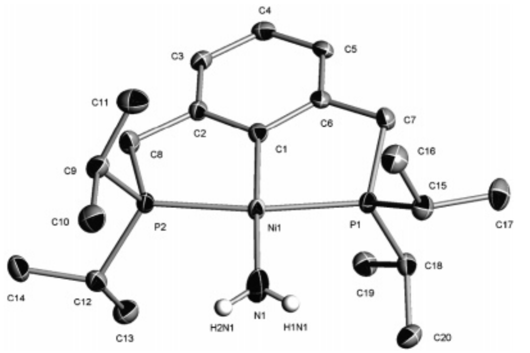


Figure 1. ORTEP diagram of Ni(PCP)(NH$_2$) (**1**). Selected bond distances (Å) (one of two independent molecules): Ni1−N1 = 1.872(2), Ni1−C1 = 1.931(2), Ni1−P1 = 2.1585(6), Ni1−P2 = 2.1587(6).

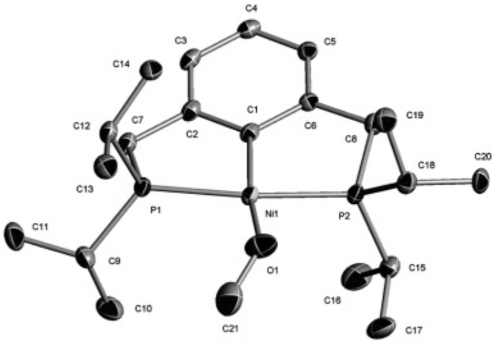


Figure 2. ORTEP diagram of Ni(PCP)(OMe) (**3**). Selected bond distances (Å) and angles (deg) (one of two independent molecules): Ni1−O1 = 1.855(2), Ni1−C1 = 1.922(3), Ni1−P1 = 2.1914(9), Ni1−P2 = 2.1543(9), O1−C21 = 1.289(5); Ni1−O1−C21 = 122.4(2).

Complex **1** is exceedingly sensitive to moisture, as it readily reacts with traces of water, forming **2** (Scheme 1). The reaction with MeOH proceeds in a similar fashion, to afford the methoxide complex Ni(PCP)(OMe) (**3**) (Scheme 1).[14] This compound is characterized by a ^{31}P{^{1}H} signal at δ 52.6 ppm and by ^{1}H and ^{13}C{^{1}H} resonances at δ 3.90 and 59.9 ppm, respectively, due to the Ni−OCH$_3$ linkage.

Very few monomeric nickel methoxides has been reported before,[15] and therefore, the structure of com-

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(8) Cámpora, J.; Palma, P.; del Río, D.; Álvarez, E. *Organometallics* **2004**, *23*, 1652.

(9) A solution of 476 mg (1 mmol) of Ni(PCP)(Br) in 30 mL of THF was added to 390 mg (10 mmol) of NaNH$_2$. The reaction mixture was sonicated for 3 h and centrifuged and the solvent removed under reduced pressure. The solid residue was extracted with hexane, the resulting suspension centrifuged, and the solvent removed under vacuum. The solid residue was extracted with hexamethyldisiloxane. The complex Ni(PCP)(NH$_2$) (**1**) was obtained as an orange crystalline solid after cooling to −30 °C. Yield: 70%.

(10) Crystal data for **1** at 100(2) K: C$_{20}$H$_{37}$NNiP$_2$, fw 412.16, monoclinic, space group $P2_1/n$, a = 10.8790(6) Å, b = 13.7440(8) Å, c = 28.7731(17) Å, α = 90°, β = 95.7910(10)°, γ = 90°, V = 4280.2(4) Å^3, Z = 8. The final r factor was 0.0422 for 10 027 independent reflections with $I > 2\sigma(I)$ (wR2 = 0.0922). GOF = 1.040.

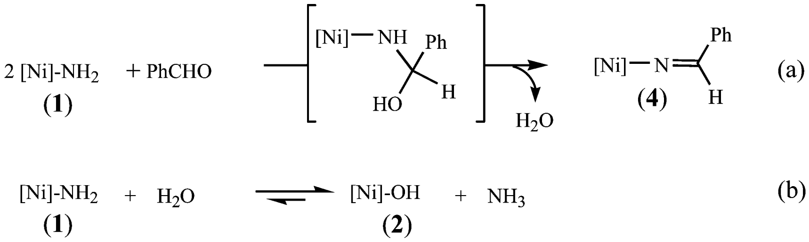
(11) Van der Lende, D. D.; Abboud, K. A.; Boncella, J. M. *Inorg. Chem.* **1995**, *34*, 5319.

(12) Mindiola, D. J.; Hillhouse, G. L.; *J. Am. Chem. Soc.* **2001**, *123*, 4623.

(13) The geometry of Ni[C$_6$H$_3$-2,6-(CH$_2$Me$_2$)$_2$](NH$_2$) was optimized using the B3LYP functional and the 6-311+G** basis set for all atoms: Ni−N = 1.883 Å, Ni−N−H(1) = 118.4°, Ni−N−H(2) = 119.2°, H(1)−N−H(2) = 105.5°.

(14) A solution of 476 mg (1 mmol) of Ni(PCP)(Br) in 30 mL of THF was added to 390 mg (10 mmol) of NaNH$_2$. The reaction mixture was sonicated for 3 h and centrifuged and the solvent removed under reduced pressure. The solid residue was extracted with hexane and the resulting suspension centrifuged again. The orange solution of complex **1** was treated with 50 μL (1.2 mmol) of MeOH, the solvent removed under vacuum, and the solid residue dissolved in hexane. Complex **3** was isolated as a dark orange crystalline solid after adding some hexamethyldisiloxane and cooling to −30 °C. Yield: 60%.

Scheme 2



plex **3** has been determined by an X-ray diffraction study.[16] Figure 2 gives an ORTEP representation of one of the two independent molecules found in the asymmetric unit. The average Ni−O bond distance, 1.856(2) Å, is only slightly shorter than that in the related hydroxide complex **2**, 1.865(2) Å.[8] The C−O bond length in complex **3**, 1.307(4) Å (average), is significantly shorter than the standard C−O bond (ca. 1.43 Å), or the distance found in early-transition-metal alkoxides. Late-transition-metal alkoxides often display anomalously short C−O bonds.[2c] It has been suggested that the shortening of the C−O distance in alkoxides bearing very polar M−O bonds is due to an attractive electrostatic interaction between the O and C atoms.[17] This effect is accompanied by an increase of the frequency of the IR C−O stretching band of **3** (1088 cm^{-1}) of 50 cm^{-1} above the standard value observed in MeOH and other methyl ethers (ca. 1030 cm^{-1}), which suggests some strengthening of the C−O bond.

Alkylamido or arylamido complexes often react with CO, giving formal insertion products.[5f] The reactivity of the parent amido complexes *trans*-$(dmpe)_2Fe(H)(NH_2)$, is somewhat different, as CO inserts into the N−H bond of the amido moiety.[5d−f] In contrast, treatment of a solution of complex **1** with dry CO (excess) or CN(2,6-$Me_2C_6H_3$) (1 equiv) in C_6D_6 solution results in the formation of complex mixtures of products that could not be identified. The formation of ammonia was detected in both cases by ^{1}H NMR spectroscopy (broad 1:1:1 triplet, δ 0.17 ppm, $^1J_{HN} = 42.0$ Hz).

The nucleophilic character of compound **1** is evidenced by its reaction with benzaldehyde. Thus, its treatment with 0.5 equiv of PhCHO (Scheme 2), yields the new aldimido complex Ni(PCP)(N=C(H)Ph) (**4**), together with equivalent amounts of **2** and NH_3. Complex **4** has been isolated from the reaction mixture, and it has been characterized by analytical and spectroscopic methods.[18] Its formation can be rationalized as shown in Scheme 2, reaction of the water generated with the excess of **1** being responsible for the formation of **2** and NH_3. Interestingly, the addition of further amounts of benzaldehyde to this reaction mixture results in the slow consumption of **2**, along with additional amounts of **4**. Since PhCHO does not react separately with the pure hydroxide or with NH_3 under the reaction conditions,[19] it seems likely that, in the presence of NH_3, the hydroxide is in equilibrium with small amounts of the amido complex, the latter reacting with benzaldehyde to produce **4**.

In summary, the first example of a parent nickel amido complex, namely Ni(PCP)(NH_2) (**1**), has been synthesized and structurally characterized. This compound reacts quantitatively with water and methanol to give the mononuclear hydroxide and methoxide derivatives Ni(PCP)(OH) (**2**) and Ni(PCP)(OMe) (**3**). In addition, it behaves as a strong nucleophile and adds rapidly to benzaldehyde, affording an equimolecular mixture of the aldimido derivative **4**, the hydroxide **2**, and ammonia. The slow formation of **4** upon addition of PhCHO to a mixture of **2** and NH_3 suggests that small amounts of the amido complex exist in equilibrium with the hydroxide and NH_3. Further studies on the reactivity of the hydroxo, amido, and alkoxo complexes of Ni and Pd are under way.

Acknowledgment. Financial support from the DGI (Project PPQ2003-000975), the Ministerio de Educación, Cultura y Deporte (research studentship, D.d.R.), and the Junta de Andalucía is gratefully acknowledged. We thank Prof. E. Carmona for helpful discussions.

Supporting Information Available: Text and tables giving experimental procedures and characterization data for all new complexes and computational details and CIF files giving X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) (a) Holland, P. L.; Andersen, R. A.; Bergman, R. G.; Huang, J.; Nolan, S. P. *J. Am. Chem. Soc.* **1997**, *119*, 12815. (b) Jian, P.; Wang, S.; Suo, J.; Wang, L.; Wu, Q. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1995**, *51*, 1071.

(16) Crystal data for **3** at 100(2) K: $C_{21}H_{38}NiOP_2$, fw 427.16, monoclinic, space group $P2_1/n$, $a = 11.0090(7)$ Å, $b = 13.8960(9)$ Å, $c = 29.403(2)$ Å, $\alpha = 90°$, $\beta = 97.7530(10)°$, $\gamma = 90°$, $V = 4457.0(5)$ Å^3, $Z = 8$. The final r factor was 0.0520 for 10 386 independent reflections with $I > 2\sigma(I)$ (wR2 = 0.0898). GOF = 1.026.

(17) Wiberg, K. B. *J. Am. Chem. Soc.* **1990**, *112*, 3379.

(18) To a solution of 150 mg (0.36 mmol) of complex **1** in 8 mL of benzene was added 74 μL (0.73 mmol) of PhCHO. The mixture was stirred overnight at room temperature and then taken to dryness and the residue extracted with hexane (10 mL). After filtration, concentration, and cooling to −30 °C several crops of orange crystals of complex **4** were isolated, some of them with a small amount of the hydroxide derivative **2**.

(19) Verified in independent experiments. Addition of NH_3 to a mixture of PhCHO and **2** causes the slow conversion of the latter in **4**.