Synthesis, Spectroscopic Characterization, and Crystal Structure of the Bimetallic Complex $[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}NH(PPh_2)_2)_2]$

Eugenio Simón-Manso,*,† Mauricio Valderrama,*,‡ Verónica Arancibia, and Yamil Simón-Manso

Departamento de Química Inorgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago, Chile

Daphne Boys

Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Casilla 487-3, Santiago, Chile

Received June 30, 1999

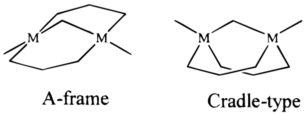
The dinuclear Ni(0) complex $[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppa)_2]$ (**1**; dppa = bis(diphenylphosphino)amine) was synthesized by two routes in good yield. Complex **1** has a triclinic crystal system and $P\bar{1}$ space group, with $a = 13.009(1)$ Å, $b = 13.063(2)$ Å, $c = 14.664(2)$ Å, $\alpha = 79.91(1)°$, $\beta = 79.96(1)°$, $\gamma = 71.32(1)°$, and $Z = 2$. The structure of this compound exhibits two μ-coordinated dppa ligands in a cis,cis arrangement. Nickel atoms are at a 2.5824(7) Å distance. Theoretical calculations predict a 0.39 bond order between metal atoms. The cyclic voltammograms show two quasi-reversible redox pairs, which correspond to the successive oxidation of the metal centers. The dinuclear complex described absorbs carbon monoxide, yielding a mixture of nickel carbonyl compounds.

Introduction

There is considerable interest in the synthesis of dinuclear complexes containing short-bite bidentate ligands as Ph_2PXPPh_2 [X = CH_2(dppm), NH(dppa); dppm = bis(diphenylphosphine)-methane ($CH_2(PPh_2)_2$); dppa = bis(diphenylphosphino)amine ($NH(PPh_2)_2$)].[1−4] In particular, the use of dppm as a bridging ligand has been studied extensively because it can form very strong metal−phosphorus bonds and can lock together the two metal atoms close to each other, promoting reactions that involve the two metal centers.[1] Dinuclear nickel complexes containing two bridging dppm ligands show either a trans,trans (A-frame complexes) or a cis,cis (cradle-type complexes) dppm conformation (Scheme 1).

Few nickel A-frame complexes have been reported showing similar coordination geometry for the two metal centers as in $[Ni_2(\mu\text{-}SO)Cl_2(dppm)_2]$ [5] or different stereochemistries as in complex $[Ni_2(\mu\text{-}CO)Cl_2(dppm)_2]$,[6] which presents a Ni−Ni bond. On the other hand, the unusual cis,cis bridging dppm arrangement is reported for $[Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2]$[7] and $[Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2]$ complexes.[8]

Scheme 1



In the synthesis of related dinuclear complexes the similar bidentate ligand dppa has received less attention. Recently, the synthesis of dinuclear gold,[9] platinum,[10] and palladium[11] complexes with a trans,trans dppa arrangement has been reported. The X-ray structures of complexes $[Pd_2(\mu\text{-}dppa)_2Cl_2]$ and $[Pd_2(\mu\text{-}dppa)_2LL'](BF_4)_2$ (L = L′ = PPh_3; L = PPh_3, L = THF) have been described.[11] In this paper we report the synthesis, crystal characterization, electrochemical behavior, and theoretical calculations of a novel dinuclear nickel(0) complex $[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppa)_2]$ that presents a cis,cis bridging dppa configuration. The relationship between electrochemical results and theoretical calculations is discussed. Also, the reaction of dinuclear nickel complex with carbon monoxide is studied.

Experimental Section

Materials and Physical Measurements. All manipulations were carried out by Schlenk tube techniques under purified nitrogen. Reagent-grade solvents were dried and distilled under nitrogen atmosphere prior to use. $Ni(CO)_4$ was purchased from a commercial source, and the ligand $NH(PPh_2)_2$ was synthesized according to a literature procedure.[12]

---

* To whom correspondence should be addressed.

† E-mail: esimon@puc.cl. Fax: 56-2-6864744.

‡ E-mail: mvalder@puc.cl. Fax: 56-2-6864744.

(1) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, 99−127.
(2) Laguna, A.; Laguna, M. *J. Organomet. Chem.* **1990**, *394*, 743−756.
(3) Bhattacharyya, P.; Woollins, J. D. *Polyhedron* **1995**, *14*, 3367−3388.
(4) Cotton, F. A. *Chem. Eng. News* **1998**, March 30, 43−46.
(5) Gong, J. K.; Fanwick, P. E.; Kubiak, C. P. *J. Chem. Soc., Chem. Commun.* **1990**, 1190−1191.
(6) Manojlivic-Muir, L.; Muir, K. W.; Davis, W. M.; Mirza, H. A.; Puddephatt, R. J. *Inorg. Chem.* **1992**, *31*, 904−909.
(7) DeLaet, D. L.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1986**, *5*, 1807−1811.
(8) Osborn, J. A.; Stanley, G. G.; Bird, P. H. *J. Am. Chem. Soc.* **1988**, *110*, 2117−2122.
(9) Usón, R.; Laguna, A.; Laguna, M.; Fraile, M. N.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1986**, 291−296.
(10) Browning, C. S.; Farrar, D. H. *J. Chem. Soc., Dalton Trans.* **1995**, 521−530.
(11) Browning, C. S.; Farrar, D. H.; Frankel, D. C.; Vittal, J. J. *Inorg. Chim. Acta* **1997**, *254*, 329−338.
(12) Wang, F. T.; Najdzionek, J.; Leneker, K. L.; Wasserman, H.; Braitsh, D. M. *Synth. React. Inorg. Metal−Org. Chem.* **1978**, *8*, 119−125.

10.1021/ic990773s CCC: $19.00

Elemental analysis (C, H, and N) was performed with a Fisons EA 1108 microanalyzer. The FTIR spectrum was recorded on a Bruker Vector-22 spectrophotometer using KBr pellets. ^1H (200 MHz) and ^{31}P(81 MHz) NMR spectra were recorded on a Bruker AC-200P spectrometer, and the chemical shifts are reported in ppm relative to Me_4Si and 85% H_3PO_4 (positive shifts downfield) in D_2O as internal and external standards, respectively. Cyclic voltammetric (CV) measurements were carried out with a potentiostat bank (model Wenking ST-72) coupled to a voltage scan generator (model USG-72) and a Graphtec recorder (model WX-1100). Bulk electrolyses were performed with a voltage integrator bank (model Wenking EVI-80). The working electrodes used in the CV and coulommetric measurements were a platinum disk and a platinum mesh, respectively. The auxiliary electrode was a platinum-coil electrode and the reference electrode a Ag/AgCl (aqueous tetramethylammonium chloride) cracked glass bead electrode, adjusted to 0.00 vs SCE. The reference electrode was located inside a Luggin capillary in the cell assembly. Electronic spectra were recorded in a Milton Roy Spectronic 3000 array spectrophotometer.

Theoretical and Computational Details. All calculations were done at a semiempirical level using a PM3 Hamiltonian, parametrized for transition metals, as implemented in the SPARTAN package.[13] Full geometry optimizations were done to obtain bond distances, bond angles, etc. for the interpretation of experimental results. It was also possible to calculate frequencies at this level of theory to ensure that the structure was a true minima, without any imaginary frequency.

The Fukui function, which measures reactivity toward nucleophilic, electrophilic, or radical agents in preferential sites,[14] is defined as

$$f(\vec{r}) = \left(\frac{\partial \rho(\vec{r})}{\partial N}\right)_{\nu} \qquad (1)$$

where $\rho(\mathbf{r})$ is the electron density and N is the number of electrons in the molecule. The derivative is taken at constant external potential. The finite-difference approximation for evaluating the Fukui function was used.

Synthesis of $[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppa)_2]$. The complex was prepared according to the two methods described below.

(i) To a solution of the ligand $NH(PPh_2)_2$ (1.0 g; 2.6 mmol) in 10 mL of benzene was added $Ni(CO)_4$ (443 mg, 2.6 mmol) dissolved in 10 mL of benzene. The solution obtained was boiled under reflux for 5 min. During this time the color of the solution changed from pale-yellow to orange and a yellow solid precipitated. The complex was filtered off, washed with pentane, and dried under vacuum. Yield, 923 mg (73%). Anal. Calcd for $C_{51}H_{42}N_2Ni_2O_3P_4$: C, 63.01; H, 4.35; N, 2.88. Found: C, 62.08; H, 4.37; N, 2.93%. IR (KBr): ν(CO) 1976, 1959, and 1789 cm^{-1}. ^{31}P NMR (298 K, $CDCl_3$-d_1): δ 72.1 (s).

(ii) To a solution of $NiCl_2{\cdot}6H_2O$ (0.5 g; 2.1 mmol) in methanol (20 mL) the ligand dppa (1.0 g; 2.1 mmol) was added. The resulting red-purple solution was saturated with carbon monoxide (1 atm) at low temperature (0 °C). A large excess of sodium tetrahydroborate (6 mmol) in methanol solution was added over a 5 min period with a constant slow flow of carbon monoxide. The black solution obtained was left at 0 °C for 8 h (1 night). The yellow solid formed was washed several times with methanol to eliminate the black suspension and then extracted with tetrahydrofuran. The complex was crystallized by addition of diethyl ether. Yield, 632 mg (50%).

X-ray Data Collection. An orange crystal, obtained from slow diffusion of *n*-hexane into a dimethyl sulfoxide solution of complex $[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppa)_2]$, having approximate dimensions of 0.36 mm × 0.26 mm × 0.1 mm, was mounted on a glass fiber. Intensity data were collected on a Siemens R3m/V diffractometer using graphite-monochromated Mo Kα radiation in $\theta/2\theta$ scan mode. Cell parameters were determined from a least-squares fit of 32 reflections with $8 \le 2\theta \le 30$. Semiempirical corrections, via ψ-scans, were applied to intensities for absorption.

Table 1. Crystallographic Data and Structure Refinement for $[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppa)_2]$

chemical formula	$C_{51}H_{42}N_2Ni_2O_3P_4$	fw	972.17
a (Å)	13.009(1)	space group	$P\bar{1}$
b (Å)	13.063(2)	temp (°C)	25
c (Å)	14.664(2)	λ (Å)	0.710 73
α (deg)	79.91(1)	ρ_{calcd} (Mg m^{-3})	1.400
β (deg)	79.96(1)	μ (Mo Kα; mm^{-1})	1.000
γ (deg)	71.32(1)	$R(F)^a$ [$F > 4\sigma(F)$]	0.0418
V (Å^3)	2305.4(5)	$R_w(F^2)^b$ (all reflns)	0.1080
Z	2		

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (0.0536P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

A riding model was used for H atoms, placed at calculated positions, with C−H and N−H distances of 0.96 and 0.90 Å, respectively, with isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameters of their parent atoms. Crystal data and relevant refinement parameters are summarized in Table 1.

Results and Discussion

The nickel tetracarbonyl complex $Ni(CO)_4$ reacts with the ligand bis(diphenylphosphino)amine [$NH(PPh_2)_2$, dppa] by refluxing in benzene to give the dinuclear complex $[Ni_2(CO)_3(dppa)_2]$ (**1**) in good yield (73%). The synthesis of the related complex $[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-}dppm)_2]$ [dppm = $CH_2(PPh_2)_2$] has been reported in the literature to be unsuccessful via this route. Therefore, the dppm complex was described to be obtained by decomposition at room temperature of the tripod compound $[Ni(CO)_2]_3HC(PPh_2)_3$[8] or from the reaction of Ni(II) salts, dppm, and $NaBH_3CN$.[15] The latter method also gave good results for the dppa ligand. Thus, the reaction of $NiCl_2{\cdot}6H_2O$ with dppa in methanol solution gave the intermediate red complex $[Ni(dppa)_2]Cl_2$, which could be reduced with $NaBH_4$ at 0 °C, with a running stream of carbon monoxide, to give complex **1**.

Complex **1** was isolated as a stable microcrystalline yellow solid; it was soluble in chloroform, benzene, tetrahydrofuran, and dimethyl sulfoxide and insoluble in polar solvents (methanol, water). These solutions slowly decompose in contact with air. The solid-state infrared spectrum in a KBr pellet shows one absorption band at 1789 cm^{-1} (very close to 1784 cm^{-1} for the analogous compound with dppm[8]) and two absorption bands at 1976 and 1959 cm^{-1}, assigned to bridge and terminal carbonyl groups, respectively. The ^{31}P NMR spectrum in deuterated chloroform shows a singlet resonance at δ 72.1 ppm.

The first synthetic procedure gives better yields. It consists of a clean reaction that forms a single product (complex **1**) and carbon monoxide, as confirmed by ^{31}P NMR spectra of the crude product of the reaction. The second method is a particularly convenient route to obtain the cradle compound and avoids the use of $Ni(CO)_4$. However, there are difficulties in separating the dinuclear complex from colloidal Ni(0), and in the subsequent elimination of other salts by methanol washing procedures.

To confirm the assumed formula and to determine the detailed geometry, an X-ray structural determination of complex **1** was undertaken. Figure 1 shows an ORTEP representation of the complex with the atom-numbering scheme. Selected bond lengths and angles (calculated and experimental) are collected in Table 2.

The molecular structure consists of two Ni−CO fragments linked by two bridging dppa ligands and a bridging carbonyl ligand. The Ni−Ni distance, 2.5824(7) Å, is consistent with a Ni−Ni single bond[8] (Ni−Ni distance in the crystal lattice of the metal is 2.487 Å at 18°[16]). Numerous measurements of metal−metal bonds in analogous zerovalent compounds of iron

---

(13) *SPARTAN DEC*, version 5.0 3X 1; Wavefunction Inc.: Irvine, CA, 1997.

(14) Parr, R. G.; Yang, W. *Density Functional of Atoms and Molecules*; Oxford Press: New York, 1989.

(15) Holah, D. G.; Hughes, A. N.; Mirza, H. A.; Thompson, J. D. *Inorg. Chim. Acta* **1987**, *126*, L7−L8.

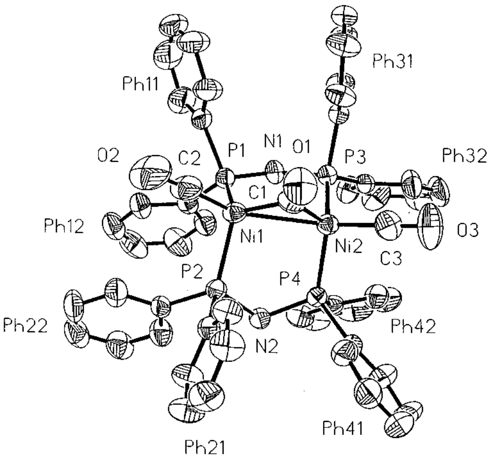


Figure 1. ORTEP plot of $[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppa})_2]$ complex with 50% thermal ellipsoids (H atoms omitted for clarity).

Table 2. Selected Experimental and Calculated Interatomic Distances (Å) and Angles (deg) for Complex $[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppa})_2]$

Distance (Å)

	exptl	calcd
Ni(1)−Ni(2)	2.5824(7)	2.5975
Ni(1)−P(1)	2.2103(9)	2.2766
Ni(1)−P(2)	2.1998(9)	2.2781
Ni(1)−C(1)	1.918(3)	1.9308
Ni(1)−C(2)	1.747(4)	1.7756
Ni(2)−P(3)	2.2097(9)	2.2795
Ni(2)−P(4)	2.2147(9)	2.2776
Ni(2)−C(1)	1.899(3)	1.9307
Ni(2)−C(3)	1.758(4)	1.7760
P(2)−N(2)	1.697(2)	1.8027
P(1)−N(1)	1.692(3)	1.8059
P(3)−N(1)	1.695(2)	1.8021
P(4)−N(2)	1.701(3)	1.8059
C(1)−O(1)	1.168(4)	1.1946
C(2)−O(2)	1.144(4)	1.1623
C(3)−O(3)	1.148(4)	1.1623

Angle (deg)

	exptl	calcd
P(2)−Ni(1)−P(1)	109.20(3)	112.25
P(3)−Ni(2)−P(4)	109.64(3)	112.27
C(2)−Ni(1)−C(1)	99.7(2)	98.90
C(3)−Ni(2)−C(1)	99.8(2)	99.05
Ni(2)−C(1)−Ni(1)	85.1(1)	85.54
P(1)−N(1)−P(3)	118.1(1)	114.91
P(2)−N(2)−P(4)	119.4(1)	114.90
Ni(1)−Ni(2)−C(3)	147.2(1)	146.49
Ni(2)−Ni(1)−C(2)	146.4(2)	146.34

and cobalt indicate that the metal−metal distances found in these compounds lie within the range of distances expected for Ni(0)−Ni(0) bonds.[17] This result was also confirmed by theoretical calculations, as described below. The structure displays unusual cis,cis bridged diphosphine ligands with the nickel centers showing a distorted tetrahedral coordination [average angles: Ni(1), 109.07° and Ni(2), 109.14°, ignoring the Ni−Ni bond]. The five-member rings Ni_2P_2N are nonplanar [deviations: Ni(1) 0.158(0), Ni(2) −0.116(0), P(2) −0.194(1), P(4) 0.047(1), N(2) 0.105(1) Å and Ni(1) 0.105(0), Ni(2) −0.172(0), P(1) −0.007(1), P(3) 0.243(1), N(1) −0.170(1) Å with respect to the mean plane] and are inclined toward each other with a dihedral angle of 77.63(3)°.

The Ni−P bond lengths [range 2.200(1)−2.215(1) Å] are slightly longer than those in the similar dppm complexes $[Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2]$ [Ni−P: average of 2.120(2) Å][8] and are similar to those found in the complex $[Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2]$[7] [Ni−P: average of 2.205(2) Å]. On the other hand, Ni−C(1) [1.899(3) and 1.918(3) Å] and Ni−C(2,3) [1.747(4) and 1.758(4) Å] are in the range of other similar carbonyl complexes.[8,18] In the bridging dppa ligands, the values of the P−N distances [average of 1.699(3) Å] and P−N−P angles [118.2(1) and 119.4(1)°] compare favorably with those found in the binuclear palladium(II) complex $[Pd_2Cl_2(\mu\text{-dppa})_2]$ [P−N, average of 1.683(6) Å; P−N−P, 116.3(4) and 117.1(3)°].[11]

Theoretical Calculation. Geometry optimization to the PM3 level gives results very close to the experimental X-ray geometry. Table 2 shows selected distances and angles for comparison of the experimental and calculated values. The coincidence between experimental and theoretical geometrical parameters is surprising for such a complex structure. It is interesting to note a slight asymmetric structure surrounding the nickel centers, as observed in the experimental and calculated results. The theoretical calculations predict a certain degree of bonding between metal centers, the bond order being approximately 0.39. A reduction of the carbon monoxide C−O bond, with respect to the free ligand, was observed. The μ-bridge carbon monoxide has a bond order of 1.87, while the CO terminals have 2.14. The electrostatic charges give a negative net charge on the nickel centers of −1.26 and −1.31 e, respectively, while phosphorus atoms have positive charges of 1.1 e.

The HOMO frontier molecular orbital reveals a strong contribution of the metal d orbitals bonding to the μ-bridge carbon monoxide and the phosphorus atoms simultaneously. Thus, the d electrons are in $d\pi$ delocalized orbitals between both metals, across the conjugated bridge ligand. This orbital is bonding with respect to Ni−C (μ-CO) bond, but it is Ni−Ni antibonding, having a nodal plane passing through the μ-CO bridge. The plane is perpendicular to the Ni−Ni axis and bisects the molecule in two symmetrical fragments. The mentioned properties of the HOMO orbital predict a moderate interaction between metal centers.

Figure 2 shows the Fukui function, $f(\vec{r})$, on the electron density surface (0.002 e/au^3) for electrophilic attack. The molecule was oriented in the same way as in Figure 1, where carbon monoxide ligands are pointing out of the paper. The Fukui function shows two symmetrical maxima between Ni−CO (μ-bridge) bonds (blue zones). Electrophilic agents, such as free carbon monoxide, prefer to attack these regions. It might lead to the formation of a new metal−ligand bond, promoting the reversible absorption of carbon monoxide to form compound **2**, as represented in Scheme 2. It is interesting to note two less intense maxima on both sides of the oxygen of the μ-bridge carbon monoxide. Isocyanide analogues show reactivity in the nitrogen atom occupying the same position as this oxygen.[7]

Cyclic Voltammetry. Figure 3 shows the cyclic voltammograms of complex **1** in THF solution. The positive scans show two quasi-reversible peaks at 0.24 and 0.51 V vs SCE (peaks a and b). Small reductions at 0.31, 0.04, −0.26, and −0.57 V vs SCE, respectively peaks c, d, e, and f, correspond to products that exist on the surface of the electrode and that were generated upon oxidation. The scan toward negative potentials shows two

---

[16] Pearson, B. W. *Lattice Spacing and Structures of Metals and Alloys*; Pergamon Press: London, 1958.

[17] Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Oxford University Press: Oxford, U.K., 1986.

[18] Einspahr, H.; Donohue, J. *Inorg. Chem.* **1974**, *13*, 1839−1843.

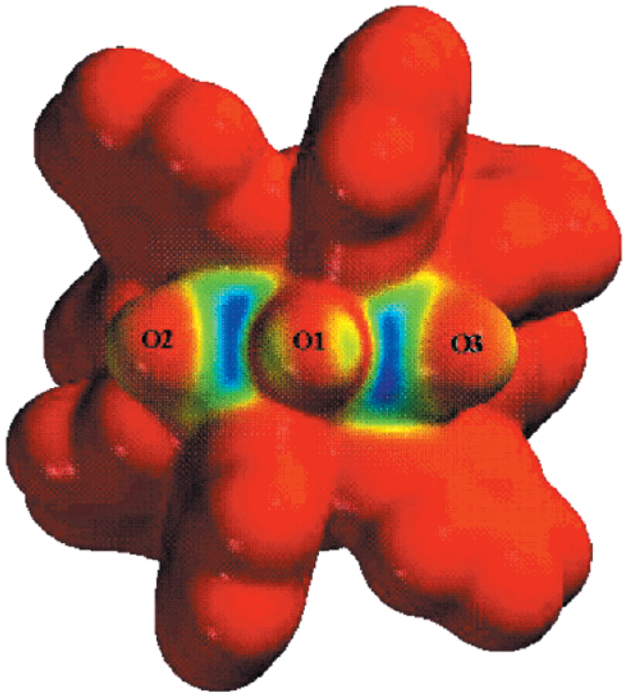
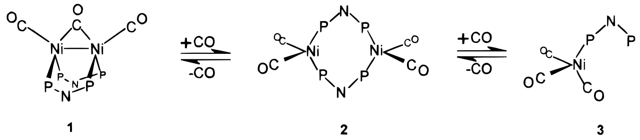


Figure 2. Fukui function plot for electrophilic attack on [$\mathrm{Ni_2}(\mu\text{-CO})(\mathrm{CO})_2(\mu\text{-dppa})_2$]. The blue color represents a maximum value for the function. Carbon monoxide ligands are pointing out of paper as in Figure 1.

Scheme 2



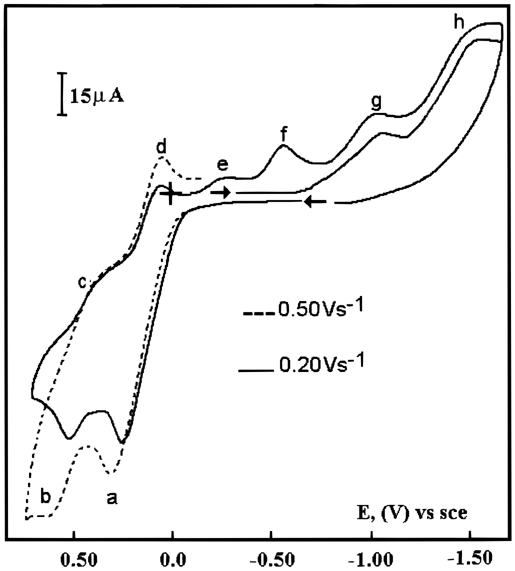


Figure 3. Cyclic voltammograms of a 3.6 mM solution of [$\mathrm{Ni_2}(\mu\text{-CO})(\mathrm{CO})_2(\mu\text{-dppa})_2$] complex in THF. Scan rate is (- - -) 0.5 and (−) 0.20 V $\mathrm{s^{-1}}$. TBATFB (10^{-3} M) is the supporting electrolyte.

irreversible reactions at −1.04 and −1.56 V vs SCE (peaks g and h), which correspond to reductions of the ligand with decomposition of the complex.

In the voltammograms an accurate measurement of the cathodic and anodic currents is difficult. Despite this, it can be seen that the i_{pc}/i_{pa} relationship is less than unity. This relation changes with scan rate, but it remains less than unity even at very high scan values (0.50 V $\mathrm{s^{-1}}$). These results suggest that the oxidation of the metal centers is coupled with a chemical reaction.[20] Cyclic voltammograms in DMSO solution show similar peak patterns and potentials; however, the i_{pc}/i_{pa} relationship is smaller than in THF, suggesting that in this solvent the oxidation product is more unstable. The oxidation peaks a and b would correspond to the consecutive oxidation of each metallic center according to the reaction

$$[\mathrm{Ni_2(CO)_3}(\mu\text{-dppa})_2]^0 \xrightleftharpoons[+\mathrm{e},\ 0.04\ \mathrm{V}]{-\mathrm{e},\ 0.24\ \mathrm{V}} [\mathrm{Ni_2(CO)_3}(\mu\text{-dppa})_2]^{1+} \xrightleftharpoons[+\mathrm{e},\ 0.31\ \mathrm{V}]{-\mathrm{e},\ 0.51\ \mathrm{V}} [\mathrm{Ni_2(CO)_3}(\mu\text{-dppa})_2]^{2+}$$

The peak separation ($\Delta E = 0.27$ V) can be explained if it is assumed that the oxidation of the first metal center produces a mixed valence compound that, according to the classification of Robin and Day,[21] would correspond to a type II compound. The most obvious manifestation of interaction between two metal centers is the separation of the two metal-centered redox potentials. Oxidation of one metal center results in a change of electron density, which is communicated to the other across the bridging; the second metal ion is affected by the additional positive charge and is therefore more difficult to oxidize than the first one.[19] The cyclic voltammetry experimental evidence of interaction between the metal centers relates well to the theoretical calculations, where a metal−metal bond order of 0.39 was calculated and where the HOMO orbital shows partial delocalization over the metal centers and bridging ligand. The oxidation process affects the electron density on this orbital, whereas the presence of a nodal plane diminishes the direct communication between both metals. Clearly, a simple one-electron orbital picture will not account for the complexity of this process, but it may support the idea that the mixed valence compound, obtained by one-electron oxidation of **1**, corresponds to a type II classification, a case between complete delocalization and nondelocalization.

The electron stoichiometry of the first oxidation process was determined by controlled potential electrolysis. The electrochemical cell was connected to a flow quartz cell to register the UV−vis spectra while the mixed-valence compound was formed. Thus, at the beginning of the oxidation an intense band appeared at 544 nm ($\epsilon = 50\,000$ $\mathrm{M^{-1}\ cm^{-1}}$), characteristic of a Ni−Ni charge transfer.[22] The magnitude of the interaction is often expressed in terms of a coupling parameter J in units of $\mathrm{cm^{-1}}$, which may be expressed as[19]

$$J = \frac{2.05 \times 10^{-2}[\epsilon \nu_{1/2} E]^{1/2}}{r} \tag{2}$$

where ϵ is the extinction coefficient for the intervalence charge transfer (IVCT) band in $\mathrm{dm^3\ mol^{-1}\ cm^{-1}}$, $\nu_{1/2}$ is the width at half-height of the IVCT band in $\mathrm{cm^{-1}}$, E is the energy of the IVCT band maximum in $\mathrm{cm^{-1}}$, and r is the metal−metal separation in Å. If the metal−metal distance does not change during the first oxidation, the coupling parameter value is $J = 69\,432$ $\mathrm{cm^{-1}}$. On the other hand the ΔE value (0.270 V) corresponds to a comproportionation constant of $K_c = 3.7 \times 10^4$ (quasi-reversible process).

---

[19] Ward, M. D. *Chem. Soc. Rev.* **1995**, *24*, 121−134.
[20] Bard, A. J.; Faulkner, L. J. *Electrochemical Methods*; Wiley: New York, 1980; Chapter 11.
[21] Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.
[22] Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: New York, 1984; Series 33.

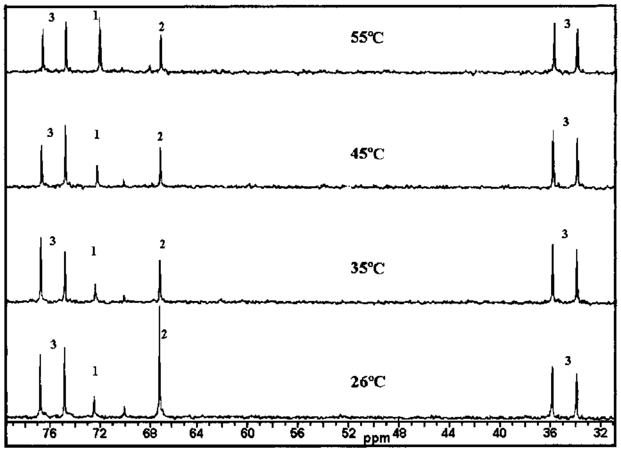


Figure 4. Variable temperature ^{31}P NMR spectra for a solution of [$Ni_2(\mu$-CO)(CO)$_2(\mu$-dppa)$_2$] in chloroform saturated with carbon monoxide.

After arriving at a maximum, the absorption decreases and the reduction peaks at 0.31 and 0.04 V are not observed, indicating that the oxidation is coupled to a chemical reaction.

Complex **1** readily reacts with carbon monoxide to yield a mixture of nickel carbonyl compounds at equilibrium (complexes **1**−**3** of Scheme 2). This reaction is reversible, and the displacement of the equilibrium was studied by monitoring the reaction by ^{31}P NMR at variable temperature. Thus, a $CDCl_3$ solution of a well-crystallized sample of compound **1** was placed into a NMR tube and saturated with carbon monoxide (25 psi at −30 °C).

Figure 4 shows the spectra recorded at different temperatures. The 26 °C spectrum shows a weak resonance at δ 72.1 ppm corresponding to the starting complex **1**, a singlet at 67.2 (2), and two doublets at 75.7 and 34.9 (3) [^2J(PP) = 150 Hz]. Warming the solution to 55 °C causes the decrease of the doublet signals and the singlet (δ 67 ppm) signal while the signal assigned to complex **1** increases in intensity. Cooling the solution to the starting temperature causes the equilibrium to shift back to species **2** and **3**, like the first recorded at this temperature. This equilibrium is reversible, and we can cycle the temperatures to regenerate the ^{31}P spectra shown. These temperature effects partially reflect the decreasing solubility of CO with the increase of temperature and, hence, displacement of the equilibrium **3** → **2** → **1**. These results are in good agreement with other equilibria reported in the literature.[8]

Attempts to isolate the mononuclear complex Ni(CO)$_3(\eta^1$-dppa) from a CO-saturated solution at low temperature (−30 °C) yield a white solid. The IR spectrum appeared as a superposition of the three compounds, with a weak band at 1789 cm^{-1} corresponding to compound **1**. Attempts to wash out the dinuclear complex from the solid with THF gave the same IR pattern. This result demonstrates that even in the solid state **2** and **3** lose CO to give **1**.

The ready and reversible uptake of CO by **1** adds another example to the small list of dinuclear complexes and clusters systems that are known to exhibit such behavior.[8,23,24]

Conclusions

The bis(diphenylphosphine)amine (dppa) ligand reacts with $Ni(CO)_4$ or $NiCl_26H_2O$ to give the dinuclear complex [$Ni_2(\mu$-CO)(CO)$_2(\mu$-dppa)$_2$] (**1**). The X-ray crystal structure of **1** confirms a cradle-type structure similar to that of bis(diphenylphosphine)methane (dppm) derivatives.

The presence of interaction between the two metal centers is demonstrated by electrochemical and UV−vis spectrochemical results. The difference between the two consecutive potentials has a value of 0.27 V. The one-electron oxidation leads to a possible formation of a mixed valence complex with a coupling parameter of $J = 69\,432$ cm^{-1}. These results are in good agreement with theoretical calculations, which predict a metal−metal bond order of 0.39, and the HOMO is bonding with respect to Ni−C (μ-CO) but is Ni−Ni antibonding.

Complex **1** reversibly reacts with carbon monoxide to give a mixture of nickel carbonyl compounds as established by ^{31}P NMR and IR spectroscopy. From a theoretical point of view, these results can be explained by an electrophilic attack on a Ni−μ(CO) bond, as was predicted by Fukui function calculations.

Acknowledgment. This work was supported by Projects Fondecyt 2980031 and Fondecyt (Lineas Complementarias) No. 8980007. E.S.M acknowledges DIPUC (Pontificia Universidad Católica de Chile) for a doctoral fellowship. We also thank Fernando Zuloaga and Barbara Loeb for helping with the theoretical calculations and revision of the manuscript.

Supporting Information Available: Tables of crystal data (atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, observed and calculated structure factors) and data from theoretical calculation (bond order matrix, electrostatic charges, distances and angles, etc.). Data in CIF format available. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990773S

---

(23) McLennan, A. J.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 811−814.

(24) Lloyd, B. R.; Bradford, A.; Puddephatt, R. J. *Organometallics* **1987**, *6*, 424−427.