

Use of 2,2'-Biphosphinines for the Stabilization of Reduced Transition Metal Species: Electrochemical Reduction of Bis(2,2'-biphosphinine)nickel(0)

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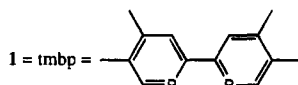
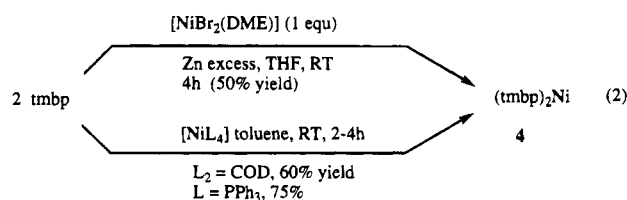
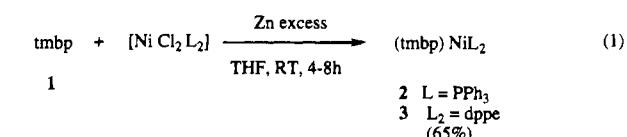
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2,2'-Bipyridines play a special role as ligands in the chemistry of reduced transition metal species¹ because of their ability to delocalize electron density from the metal centers over their pyridine rings. Previously, we have shown that the mono-electronic reduction of a 2,2'-biphosphinine is substantially easier than that of the corresponding bipyridine, which implies that they should be better candidates for stabilizing reduced metallic species than their nitrogen-containing counterparts. Here, we verify the validity of this hypothesis in the case of a bis(2,2'-biphosphinine)nickel(0) complex.

A series of nickel(0) complexes of 4,4',5,5'-tetramethyl-2,2'-biphosphinine (tmbp) **1**² was first prepared according to eqs 1 and 2.



These complexes (2–4) were characterized by ¹H, ¹³C, ³¹P NMR spectroscopy and, when sufficiently stable,³ by elemental analyses. Unlike [Ni(bpy)₂],⁴ complex **4** is stable to air. Its low solubility in common organic solvents precluded the recording of a ¹³C NMR spectrum, but toluene yielded good single crystals, which revealed a distorted tetrahedral structure⁵ (Figure 1) having a P₁NiP₁₂/P₁₃NiP₂₄ interplane angle of 74.38 ± 0.03°. The P–Ni bond lengths are significantly longer in **4** (2.141–2.149(1) Å) than in the tetrakis(phosphinine)nickel complex [Ni(C₅H₅P)₄]⁶ (2.1274(5) Å), probably because of the decrease in the P–Ni–P angle, which falls from 109 to 85° in **4**. The phosphorus-carbon bonds which form the P–C–C–P bridge of **4** (1.740–1.748(4) Å) are relatively long by com-

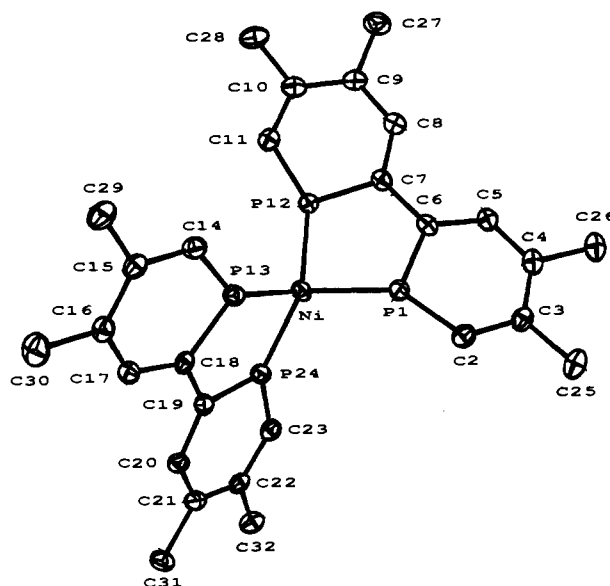
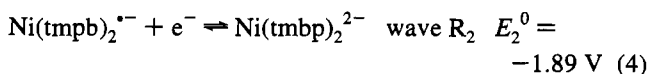
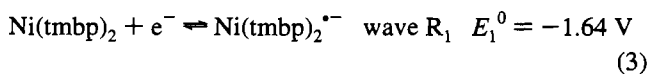


Figure 1. ORTEP drawing of one molecule of **4**. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) are as follows: Ni–P(1) = 2.141(1), P(1)–C(2) = 1.711(4), P(1)–C(6) = 1.744(4), C(6)–C(7) = 1.464(5). Bond angles (deg): P(1)–Ni–P(12) = 85.29(4), P(1)–Ni–P(13) = 130.77(4).

parison with the external P–C distances (1.711–1.722(4) Å) or with the P–C ring bonds in [Ni(C₅H₅P)₄]⁶ (1.714–1.718(2) Å). Additionally, we notice an interesting correlation between the electron-accepting character of the transition metal center and the opening of the ∠CPC angle of the phosphinine nucleus: mean ∠CPC (deg) = 1, 100.5;² [Ni(1)₂], 102.5; [Cr(CO)₄(1)], 104.3;⁷ [RuCl₂(1)(dmsO)₂], 106.08.⁸ Otherwise, the structural parameters of the biphosphinine in **4** are very similar to those found in other complexes.^{7,8}

An electrochemical study of the reduction of **4** was undertaken to evaluate the electron accepting capacity of the coordinated biphosphinine. Scanning to negative values from the rest potential (–0.02 V vs SCE), revealed four reduction peaks. Two reversible mono-electronic reduction waves⁹ (Figure 2a) at $E_{\text{PR}1} = -1.680$ V and $E_{\text{PR}2} = -1.920$ V and two tiny irreversible reduction waves at $E_{\text{PR}3} = -2.315$ V and $E_{\text{PR}4} = -2.550$ V (Figure 2c). The two first waves are the two successive mono-electronic reductions of the coordinated biphosphinine (Figure 2b) in the complex affording Ni(tmbp)₂^{•–} and Ni(tmbp)₂^{2–} species (eqs 3 and 4).



The identity of the irreversible minor waves R₃ and R₄, was established by cyclic voltammetry of the free ligand (previously

(1) See for example: Kaim, W. *Coord. Chem. Rev.* **1987**, 76, 187.
(2) Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F.; Jutand, A.; Amatore, C. *Organometallics* **1992**, 11, 2475.
(3) ³¹P NMR (THF): δ 191.37 (t, ²J_{PP} = 26.5 Hz, ring P), 39.25 (t, PPh₃). Complex **2** is rather labile. ³¹P NMR (C₆D₆): δ 189.94 (t, ²J_{PP} = 25.2 Hz, ring P), 53.25 (t, dppe). Anal. Calcd for C₄₀H₄₀P₄Ni: C, 68.30; H, 5.73. Found: C, 68.70; H, 5.42. **4**. ³¹P NMR: (CDCl₃) δ 190.40; (THF) δ 194.90. Anal. Calcd for C₂₈H₃₂P₄Ni: C, 61.02; H, 5.85. Found: C, 61.35; H, 5.66.
(4) Henne, B. J.; Bartak, D. E. *Inorg. Chem.* **1984**, 23, 369.

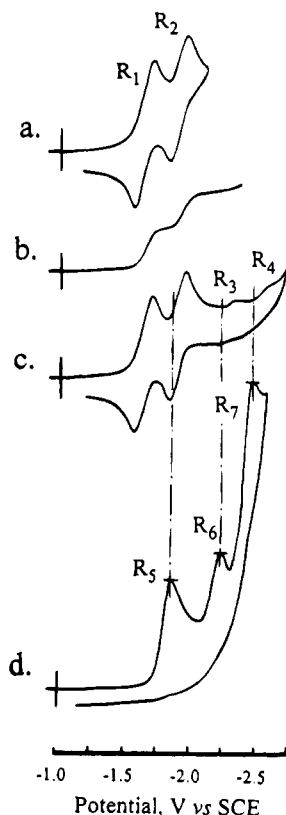
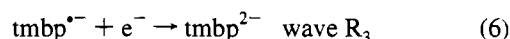
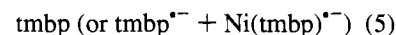
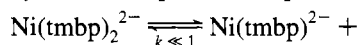


Figure 2. (a) Cyclic voltammetry of **4**, 2 mM in THF/*n*-Bu₄NBF₄ (0.3 M) at a stationary gold disk electrode (0.5-mm diameter): scan rate 0.2 V·s⁻¹; 20 °C. (b) Stationary gold disk ultramicroelectrode (0.25 μm); scan rate 0.020 V·s⁻¹; 20 °C. (c) Same conditions but the scan has been extended up to -2.7 V. (d) Cyclic voltammetry of **1**, 2 mM in THF/*n*-Bu₄NBF₄ (0.3 M) at a stationary gold disk electrode (0.5-mm diameter): scan rate 0.2 V·s⁻¹; 20 °C.

described in DMF)² in the same experimental conditions ($E_{\text{P}R5} = -1.86_8$ V, $E_{\text{P}R6} = -2.24_1$ V, and $E_{\text{P}R7} = -2.47_9$ V). A comparison between the two voltammograms (Figure 2c,d) and our earlier results led us to ascribe these two peaks to the formation of the dianion tmbp^{2-} (eq 6) and to the reduction of its protonated product respectively; the free ligand or its anion radical being produced by the exergonic ($\Delta G^0 < 0$) reversible dissociation of $\text{Ni}(\text{tmbp})_2^{2-}$ according to eq 5. Additionally, these experiments also conclusively eliminate the possibility that the reduction peak R₂ is the reduction of the free ligand

(compare the low peak current of R₃ relative to that of R₂ in the complex and the peak current of R₆ to that of R₅ in the free ligand).

According to cyclic voltammetry, the $\text{Ni}(\text{tmbp})_2^{2-}$ complex has a half-life time of approximately 15 s. Nonetheless, this value is grossly underestimated since the magnitude of the plateau shaped wave R₃ does not represent a thermodynamic, but a dynamic flux because of the electrochemical displacement of the endergonic equilibrium¹⁰ (5) to its right hand side induced by the consumption of $\text{tmbp}^{\bullet-}$ in the diffusion layer (see eq 6).



A comparison of these results with those obtained in the electrochemical study of the $\text{Ni}(\text{bpy})_2^{4+}$ complex reveals some important information. First, the first mono-electronic reduction of the biphosphinine complex is easier by 0.29 V with respect to its nitrogen counterpart ($E_{\text{P}c} = -1.97$ V vs SCE in MeCN). This positive shift is expected owing to the better π -accepting ability of the biphosphinine^{2,8} compared to bipyridine. Additionally, this difference should be increased where the ligands have the same substitution scheme (unsubstituted biphosphinine or tetramethyl bipyridine).

Second, the full reversibility of the first reduction peak demonstrates that the $\text{Ni}(\text{tmbp})_2^{2-}$ complex is stable within the time scale of the cyclic voltammetry, whereas the bipyridine ligand was reported to be labile in the $\text{Ni}(\text{bpy})_2^{\bullet+}$ species.⁴

To date, there appears no evidence for the stability of a $\text{Ni}(\text{bpy})_2^{2-}$ species. Earlier experiments⁴ suggest that, under reduction, the $\text{Ni}(\text{bpy})_2^{\bullet-}$ anion radical complex undergoes dissociation of a bpy ligand to give an unstable solvated complex which has been formulated as $\text{Ni}(\text{bpy})(\text{MeCN})_2^{2-}$ ($t_{1/2} = 1$ s), whilst reduction in the presence of an excess bipyridine yields only Ni^0 and the bipyridine anion radical by an irreversible reaction. Therefore, it may be concluded from this comparison that biphosphinines are more efficient than bipyridines for the stabilization of electron excessive metal centers. This work is being extended on other reduced metallic centers.

Acknowledgment. We thank CNRS, Ecole Polytechnique and ENS for supporting this work.

Supplementary Material Available: X-ray structure determination for **4**, including tables of crystal data, positional parameters, bond distances and angles for all non-hydrogen atoms, β_{ij} values, least-squares planes, and torsion angles (8 pages). Ordering information is given on any current masthead page.

- (5) X-ray structure determination for **4**: Crystals of **4**, C₂₈H₃₂NiP₄, were grown from a warm toluene solution of the compound. Data were collected at -150 ± 0.5 °C on an Enraf Nonius CAD4 diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The crystal structure was solved and refined using the Enraf Nonius MOLEN package. The compound crystallizes in space group P1 (No. 2), $a = 11.524(1)$ Å, $b = 14.886(1)$ Å, $c = 8.239(1)$ Å, $\alpha = 90.84(1)^\circ$, $\beta = 100.18(1)^\circ$, $\gamma = 109.61(1)^\circ$; $V = 1306.24(50)$ Å³; $Z = 2$; $d_{\text{calc}} = 1.401$ g/cm³; $\mu = 10.0$ cm⁻¹; $F(000) = 576$. A total of 5698 unique reflections were recorded in the range $2^\circ \leq 2\theta \leq 54.0^\circ$ of which 1399 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 4299 for solution and refinement. Direct methods yielded a solution for the four phosphorus and the nickel atoms. The hydrogen atoms were included as fixed contributions in the final stages of least-squares refinement while using anisotropic temperature factors for all other atoms. A non-Poisson weighting scheme was applied with a p factor equal to 0.08. The final agreement factors were $R = 0.049$, $R_w = 0.071$, and $\text{GOF} = 1.46$.
- (6) Elschenbroich, C.; Nowotny, M.; Behrendt, A.; Massa, W.; Wocadlo, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1343.

- (7) Le Floch, P.; Carmichael, D.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1991**, *113*, 667.
- (8) (a) Carmichael, D.; Le Floch, P.; Ricard, L.; Mathey, F. *Inorg. Chim. Acta* **1992**, *198*–200, 437. (b) Elschenbroich, C.; Nowotny, M.; Kroker, J.; Behrendt, A.; Massa, W.; Wocadlo, S. *J. Organomet. Chem.* **1993**, *459*, 157.
- (9) $n_{R1} = 0.99 \pm 0.05$ and $n_{R2} = 1.03 \pm 0.05$ absolute numbers determined according to: Amatore, C.; Azzabi, M.; Calas, P.; Jutand, A.; Lefrou, C.; Rollin, Y. *J. Electroanal. Chem.* **1990**, *288*, 45–63.
- (10) Besides the characteristic plateau shape of the waves, the involvement of a CE mechanism is also apparent from the half-wave potential shift toward more negative values than those of the free ligand (compare E_{R3} vs E_{R6} and E_{R4} vs E_{R7}). (a) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; pp 443–449. (b) Amatore, C.; Azzabi, M.; Jutand, A. *J. Am. Chem. Soc.* **1991**, *113*, 1670.