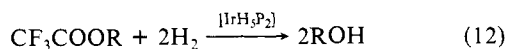
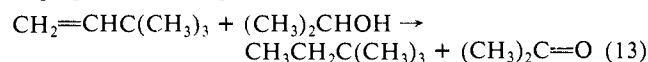


reaction intermediate  $[\text{IrH}_3\text{P}_2]$  (eq 5-7) by rapid conversion of both  $[\text{IrH}_3\text{P}_2]$  and  $[\text{IrH}_2\text{P}_2(\text{OR})]$  to  $[\text{IrH}_3\text{P}_2]$ .



While the behavior cited above would appear to limit the utility of  $[\text{IrH}_3\text{P}_2]$  as a hydrogenation catalyst with use of  $\text{H}_2$ , the chemistry that we have identified should be conducive to pathways for transfer hydrogenation.<sup>12</sup> In accord with this we have found that  $[\text{IrH}_3\text{P}_2]$ , indeed, is a very efficient catalyst or catalyst precursor for the transfer hydrogenation of *tert*-butylethylene by isopropyl alcohol (eq 13).



At 30 °C, with initial concentrations of 0.12 M  $\text{CH}_2=\text{CHC}(\text{CH}_3)_3$ , 0.60 M  $(\text{CH}_3)_2\text{CHOH}$ , and  $5.0 \times 10^{-3}$  M  $[\text{IrH}_3\text{P}_2]$ , reaction 13 exhibited autocatalytic kinetics and was essentially complete in ca. 50 min. Initial addition of 0.2 M  $(\text{CH}_3)_2\text{C}=\text{O}$  eliminated the induction period and reaction was complete in less than 10 min. To our knowledge this is the most active transfer olefin hydrogenation catalyst that has been reported to date.<sup>13</sup> The mechanistic features of this system are being investigated.

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(11) The analogous  $[\text{IrH}_3(\text{PEt}_2\text{Ph})_2(\text{CO})]$  complex has been reported: Mann, B. E.; Masters, C.; Shaw, B. L. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2195-2204.

(12) (a) Brieger, G.; Nestruck, T. *J. Chem. Rev.* **1974**, *74*, 567-580, and references cited therein. (b) Kolomnikov, I. S.; Kukolev, V. P.; Vol'pin, M. E. *Russian Chem. Revs.* **1974**, *43*, 399-413 and references cited therein.

(13) At much higher temperatures (100-150 °C),  $[\text{IrH}_4\text{P}_2]$  also has been reported to serve as a slow catalyst or catalyst precursor for the hydrogenation of *tert*-butylethylene by saturated hydrocarbons such as cyclooctane or methylcyclohexane.<sup>14</sup>

(14) (a) Felkin, H.; Fillebeen-Kahn, T.; Gault, Y.; Holmes-Smith, R.; Zakrzewski, J. *Tetrahedron Lett.* **1984**, *25*, 1279-1282. (b) Felkin, H.; Fillebeen-Kahn, T.; Holmes-Smith, R.; Yingrui, L. *Ibid.* **1985**, *26*, 1999-2000.

## The Reaction of $(\text{Cy}_3\text{P})_2\text{Ni}(\text{H})(\text{CH}_3)$ with Carbon Dioxide. Formation of a Hydridonickel Formate Complex, $\text{HNi}(\text{O}_2\text{CH})(\text{Cy}_3\text{P})_2$

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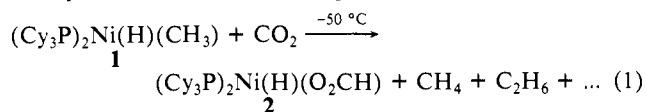
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Chemists have been impressed by the Halpern axiom that observations of "likely" intermediates in a catalytic cycle generally signal, in fact, a nonproductive, sluggish, loop of the pathway.<sup>1</sup> Nevertheless, there remains intellectual satisfaction from chasing compounds of a catalytically active metal, ligand modified to stabilize a possible model intermediate. Of the few nickel complexes amenable for study of the carbon dioxide methanation process<sup>2</sup> are derivatives of Ni(II) and tricyclohexylphosphine ( $\text{PCy}_3$ ). First synthesized by Jonas and Wilke, *trans*- $(\text{Cy}_3\text{P})_2\text{Ni}(\text{H})(\text{CH}_3)$ , **1**, is unstable to light and heat and slowly

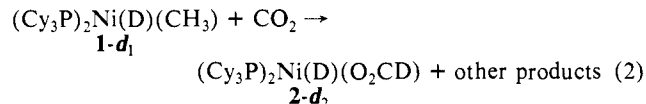
decomposes even in the solid state giving off methane.<sup>3,4</sup> Species of this type can also serve as intermediates for C-H/ $\text{CO}_2$  activation processes.<sup>5</sup>

As a solution in benzene or toluene **1** reacts swiftly with 1 atm of carbon dioxide even at -50 °C, accompanied by a color change from yellow to orange-brown (eq 1). When employing labeled



<sup>13</sup>C<sub>2</sub>O<sub>2</sub> the reaction was readily monitored by <sup>13</sup>C{<sup>1</sup>H} NMR. At -50 °C the major metal-containing product (ca. 35%) detected was *trans*- $(\text{Cy}_3\text{P})_2\text{Ni}(\text{H})(\text{O}_2\text{CH})$ , **2**, which was separated by chromatography on a silica gel column and recrystallized several times from hexane/THF. Product **2** was identified by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR, IR, and elemental analysis.<sup>6,7</sup> Compound **2** may be prepared selectively and in high yield upon direct addition of  $\text{HCO}_2\text{H}$  to  $\{(\text{Cy}_3\text{P})_2\text{Ni}\}_2\text{N}_2$  analogous to the synthesis of  $(\text{Cy}_3\text{P})_2\text{Ni}(\text{H})(\text{OAc})$ .<sup>4</sup> During the course of reaction 1 methane and ethane gases (ca. 4:1 ratio) evolved and were detected by gas chromatography. A yet unidentified product (ca. 30%) gave rise to a signal at 169.0 ppm in the carboxylate region of the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum and a <sup>1</sup>H signal in the Ni-CH<sub>3</sub> region at -0.58 ppm. Thus far, we have not been able to separate this compound, a product of the primary reaction, in pure form by column chromatography. Indeed this product may be the straightforward result of  $\text{CO}_2$  insertion into the Ni-H bond of **1** with formation of  $(\text{Cy}_3\text{P})_2\text{Ni}(\text{CH}_3)\text{O}_2\text{CH}$ . Further support for this suggestion is provided by the reaction of the phenyl analog of **1**,  $(\text{Cy}_3\text{P})_2\text{Ni}(\text{H})(\text{Ph})$ , **3**, with carbon dioxide yielding  $(\text{Cy}_3\text{P})_2\text{Ni}(\text{Ph})(\text{O}_2\text{CH})$  (vide infra). Another low yield, organometallic product was observed when the reaction was carried out above 0 °C. Consistent with the <sup>13</sup>C, <sup>31</sup>P, and <sup>1</sup>H NMR and supported by elemental analysis, this product is formulated as the dimer  $(\text{CH}_3)(\text{Cy}_3\text{P})\text{Ni}(\text{O}_2\text{CO})\text{Ni}(\text{H})(\text{PCy}_3)_2$ ,<sup>8</sup> which results from reaction with wet  $\text{CO}_2$ , similar to the dimetallic carbonate complexes reported in the literature.<sup>9-11</sup>

Upon preparing the Ni-D version of **1**, carboxylation produces **2** with deuterium in both the hydride and the formate positions as shown by <sup>2</sup>H{<sup>1</sup>H} NMR, eq 2. Furthermore, no ethylene or



(3) Jolly, P. W.; Jonas, K.; Krueger, C.; Tsay, Y.-H. *J. Organomet. Chem.* **1971**, *33*, 109.

(4) Jonas, K.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 519.

(5) Ito, T.; Yamamoto, A. *Organic and Bio-Organic Chemistry of Carbon Dioxide*; Inoue, S., Yamazaki, N., Eds.; Kodansha, Ltd.: Tokyo, 1982; p 79.

(6) Recrystallization of **2** at -10 °C gives an analytically pure yellow substance: <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ , 23 °C)  $\delta$  8.90 (s, Ni-O<sub>2</sub>CH),  $\delta$  -27.59 (t, Ni-H,  $J_{\text{H-P}} = 77$  Hz); <sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{C}_6\text{D}_6$ , 23 °C)  $\delta$  166.7 (s, Ni-CO<sub>2</sub>H); <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{C}_6\text{D}_6$ , 23 °C)  $\delta$  33.47 (d,  $J_{\text{C-P}} = 67.9$  Hz,  $\text{PCy}_3$ ); IR (KBr cell)  $\text{CO}_2$  adsorption at 1619 and 1310  $\text{cm}^{-1}$ ,  $\nu_{\text{Ni-H}}$  at 1931  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{37}\text{H}_{68}\text{O}_3\text{P}_2\text{Ni}$ : C, 66.4; H, 10.2; P, 8.9; Ni, 8.8. Found: C, 66.8; H, 10.6; P, 8.9; Ni, 8.3. The platinum analogue of **2**, *trans*-PtH(O<sub>2</sub>CH)[P(C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>]<sub>2</sub>, has been characterized by X-ray crystallography.<sup>7</sup>

(7) Immerzi, A.; Musco, A. *Inorg. Chim. Acta* **1977**, *22*, L35.

(8) Repeated recrystallization from hexane at -10 °C yielded a yellow powder of constant composition of ca. 80% **3** and 20% **2**. Anal. Calcd for 80%  $\text{C}_{58}\text{H}_{103}\text{O}_3\text{P}_3\text{Ni}_2$  and 20%  $\text{C}_{37}\text{H}_{68}\text{O}_3\text{P}_2\text{Ni}$ : C, 61.4; H, 9.5; P, 8.5; Ni, 10.2; found: C, 62.5; H, 9.8; P, 7.8; Ni, 9.5. Spectroscopic data subtracted from **2**: <sup>1</sup>H NMR ( $\text{C}_6\text{D}_6$ , 23 °C)  $\delta$  -0.47 (d,  $J_{\text{H-P}} = 4.1$  Hz, Ni-CH<sub>3</sub>),  $\delta$  -28.45 (t,  $J_{\text{H-P}} = 76.5$  Hz, Ni-H); <sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{C}_6\text{D}_6$ , 23 °C)  $\delta$  170.6 (s, Ni-O<sub>2</sub>CO-Ni); <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{C}_6\text{H}_6$ , 23 °C)  $\delta$  44.0 (s, Ni-P<sub>2</sub>),  $\delta$  32.5 (d,  $J_{\text{P-C}} = 68.5$  Hz, Ni-P<sub>6</sub>); IR 1580  $\text{cm}^{-1}$ .

(9) Deliberate addition of H<sub>2</sub>O yielded the dimer as a major product with spectral properties similar to those reported for  $(\text{CH}_3\text{CMe}_2\text{Ph})(\text{PMe}_3)\text{Ni}(\text{O}_2\text{CO})\text{Ni}(\text{CH}_3\text{CMe}_2\text{Ph})(\text{PMe}_3)_2$  (IR (Nujol mull)  $\text{CO}_3$  at 1505  $\text{cm}^{-1}$ ; <sup>13</sup>C{<sup>1</sup>H} NMR ( $\text{C}_6\text{D}_6$ , 21 °C)  $\delta$  170.4 (s,  $\text{CO}_3$ ) has been reported: Carmona, E.; Palma, P.; Paneque, M.; Poveda, M. L.; Gutierrez-Puebla, E.; Monge, A. *J. Am. Chem. Soc.* **1986**, *108*, 6424.

(10) Yoshida, T.; Thorn, D. L.; Okano, T.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 4212.

(11) Krogsrud, S.; Komiya, S.; Ito, T.; Ibers, J. A.; Yamamoto, A. *Inorg. Chem.* **1976**, *15*, 2798.

<sup>†</sup> On leave of absence from the University of Malaya, Kuala Lumpur, Malaysia.

(1) Halpern, J. *Science (Washington, D.C.)* **1982**, *217*, 401.

(2) Darensbourg, D. J.; Bauch, C. G.; Ovalles, C. *Rev. Inorg. Chem.* **1985**, *7*, 315.

