reaction intermediate $[IrH_3P_2]$ (eq 5–7) by rapid conversion of both $[IrH_3P_2]$ and $[IrH_2P_2(OR)]$ to $[IrH_5P_2]$.

$$CF_3COOR + 2H_2 \xrightarrow{[IrH_5P_2]} 2ROH \qquad (12)$$

While the behavior cited above would appear to limit the utility of $[IrH_5P_2]$ as a hydrogenation catalyst with use of H_2, the chemistry that we have identified should be conducive to pathways for transfer hydrogenation.[12] In accord with this we have found that $[IrH_5P_2]$, indeed, is a very efficient catalyst or catalyst precursor for the transfer hydrogenation of *tert*-butylethylene by isopropyl alcohol (eq 13).

$$CH_2{=}CHC(CH_3)_3 + (CH_3)_2CHOH \rightarrow CH_3CH_2C(CH_3)_3 + (CH_3)_2C{=}O \qquad (13)$$

At 30 °C, with initial concentrations of 0.12 M $CH_2{=}CH{-}C(CH_3)_3$, 0.60 M $(CH_3)_2CHOH$, and 5.0×10^{-3} M $[IrH_5P_2]$, reaction 13 exhibited autocatalytic kinetics and was essentially complete in ca. 50 min. Initial addition of 0.2 M $(CH_3)_2C{=}O$ 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.[13] The mechanistic features of this system are being investigated.

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(11) The analogous $[IrH_3(PEt_2Ph)_2(CO)]$ complex has been reported: Mann, B. E.; Masters, C.; Shaw, B. L. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2195–2204.

(12) (a) Brieger, G.; Nestrick, 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), $[IrH_5P_2]$ 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.[14]

(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 $(Cy_3P)_2Ni(H)(CH_3)$ with Carbon Dioxide. Formation of a Hydridonickel Formate Complex, $HNi(O_2CH)(Cy_3P)_2$

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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.[1] 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[2] are derivatives of Ni(II) and tricyclohexylphosphine (PCy_3). First synthesized by Jonas and Wilke, *trans*-$(Cy_3P)_2Ni(H)(CH_3)$, **1**, is unstable to light and heat and slowly decomposes even in the solid state giving off methane.[3,4] Species of this type can also serve as intermediates for $C{-}H/CO_2$ activation processes.[5]

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

$$\underset{\mathbf{1}}{(Cy_3P)_2Ni(H)(CH_3)} + CO_2 \xrightarrow{-50\ ^\circ C} \underset{\mathbf{2}}{(Cy_3P)_2Ni(H)(O_2CH)} + CH_4 + C_2H_6 + \ldots \qquad (1)$$

$^{13}CO_2$ the reaction was readily monitored by $^{13}C\{^1H\}$ NMR. At −50 °C the major metal-containing product (ca. 35%) detected was *trans*-$(Cy_3P)_2Ni(H)(O_2CH)$, **2**, which was separated by chromatography on a silica gel column and recrystallized several times from hexane/THF. Product **2** was identified by ^1H, ^{13}C, and ^{31}P NMR, IR, and elemental analysis.[6,7] Compound **2** may be prepared selectively and in high yield upon direct addition of HCO_2H to $\{(Cy_3P)_2Ni\}_2N_2$ analogous to the synthesis of $(Cy_3P)_2Ni(H)(OAc)$.[4] 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 $^{13}C\{^1H\}$ NMR spectrum and a ^1H signal in the $Ni{-}CH_3$ 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 CO_2 insertion into the Ni–H bond of **1** with formation of $(Cy_3P)_2Ni(CH_3)O_2CH$. Further support for this suggestion is provided by the reaction of the phenyl analog of **1**, $(Cy_3P)_2Ni(H)(Ph)$, **3**, with carbon dioxide yielding $(Cy_3P)_2Ni(Ph)(O_2CH)$ (vide infra). Another low yield, organometallic product was observed when the reaction was carried out above 0 °C. Consistent with the ^{13}C, ^{31}P, and ^1H NMR and supported by elemental analysis, this product is formulated as the dimer $(CH_3)(Cy_3P)Ni(O_2CO)Ni(H)(PCy_3)_2$,[8] which results from reaction with wet CO_2, similar to the dimetallic carbonate complexes reported in the literature.[9-11]

Upon preparing the Ni–D version of **1**, carboxylation produces **2** with deuterium in both the hydride and the formate positions as shown by $^2H\{^1H\}$ NMR, eq 2. Furthermore, no ethylene or

$$\underset{\mathbf{1}\text{-}\boldsymbol{d}_1}{(Cy_3P)_2Ni(D)(CH_3)} + CO_2 \rightarrow \underset{\mathbf{2}\text{-}\boldsymbol{d}_2}{(Cy_3P)_2Ni(D)(O_2CD)} + \text{other products} \qquad (2)$$

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† 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.

(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., Yamozaki, N., Eds.; Kodonsha, Ltd.: Tokyo, 1982; p 79.

(6) Recrystallization of **2** at −10 °C gives an analytically pure yellow substance: ^1H NMR (C_6D_6, 23 °C) δ 8.90 (s, $Ni{-}O_2CH$), δ −27.59 (t, Ni–H, J_{H-P} = 77 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6, 23 °C) δ 166.7 (s, $Ni{-}CO_2H$); $^{31}P\{^1H\}$ NMR (C_6D_6, 23 °C) δ 33.47 (d, J_{C-P} = 67.9 Hz, PCy_3); IR (KBr cell) CO_2 adsorption at 1619 and 1310 cm^{-1}, ν_{Ni-H} at 1931 cm^{-1}. Anal. Calcd for $C_{37}H_{68}O_2P_2Ni$: 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*-$PtH(O_2CH)[P(C_6H_{11})_3]_2$, has been characterized by X-ray crystallography.[7]

(7) Immirzi, 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% $C_{56}H_{103}O_3P_3Ni_2$ and 20% $C_{37}H_{68}O_2P_2Ni$: 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**: ^1H NMR (C_6D_6, 23 °C) δ −0.47 (d, J_{H-P} = 4.1 Hz, $Ni{-}CH_3$), δ −28.45 (t, J_{H-P} = 76.5 Hz, Ni–H); $^{13}C\{^1H\}$ NMR (C_6D_6, 23 °C) δ 170.6 (s, $Ni{-}O_2CO{-}Ni$); $^{13}P\{^1H\}$ NMR (C_6H_6, 23 °C) δ 44.0 (s, $Ni{-}P_a$), δ 32.5 (d, J_{P-C} = 68.5 Hz, $Ni{-}P_b$); IR 1580 cm^{-1}.

(9) Deliberate addition of H_2O yielded the dimer as a major product with spectral properties similar to those reported for $(CH_2CMe_2Ph)(PMe_3)Ni(O_2CO)Ni(CH_2CMe_2Ph)(PMe_3)_2$(IR (Nujol mull) CO_3 at 1505 cm^{-1}; $^{13}C\{^1H\}$ NMR (C_6D_6, 21 °C) δ 170.4 (s, 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.

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hydrogen gases were evolved. This leads to the conclusion that the hydride and formate hydrogens in **2** originate exclusively from the hydride in **1** and that the methyl group maintains its integrity. Potential sinks for the methyl group other than those observed include methyl acetate for which there is ^{13}C NMR spectral evidence. Efforts are continuing to more fully characterize reaction 1, both chemically and mechanistically.

Whereas reductive elimination of CH_4 from **1** was readily induced by ambient lighting or by addition of a donor ligand such as CO, compound **2** was stable under these conditions.[12] In fact neither reductive elimination nor decarboxylation occurred after prolonged heating at 50 °C. Even so, when **2** is dissolved in benzene-d_6 under 1 atm $^{13}CO_2$, carbon dioxide is incorporated as shown in eq 3. At 22 °C the half-life for this reaction is about 150 min.

$$\mathrm{(Cy_3P)_2Ni(H)(O_2CH)} + {}^{13}\mathrm{CO_2} \rightleftarrows \mathrm{(PCy_3)_2Ni(H)(O_2{}^{13}CH)} + {}^{12}\mathrm{CO_2} \qquad (3)$$

The preparation of **2-*d*₁**, from the reaction of $\{(Cy_3P)_2Ni\}_2N_2$ and HCOOD,[13] permitted a study of the rate of the exchange process described in eq 4. Interestingly, this equilibrium between

$$\underset{\mathbf{2\text{-}}\boldsymbol{d}_1}{\mathrm{(Cy_3P)_2Ni(D)(O_2CH)}} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\mathbf{2\text{-}}\boldsymbol{d}'_1}{\mathrm{(PCy_3)_2Ni(H)(O_2CD)}} \qquad (4)$$

2-*d*₁ and **2-*d*′₁** was achieved in the solid state after ca. 7 days. When in solution the equilibrium is attained with an equal distribution of deuterium between hydride and formate positions. The reaction is first-order in complex **2** with a $t_{1/2}$ for progress toward equilibrium of 510 min. Since both $^{13}CO_2/CO_2$ exchange in (3) and H/D exchange in (4) may proceed by way of CO_2 extrusion and a $Ni(H)_2$ intermediate, it is possible that the two reactions are related. It has not been possible to prepare the dihydride species from $[(Cy_3P)_2Ni]_2N_2$ and H_2; however, alternative synthetic routes to this species are being pursued.[14] At this juncture it is not clear that the difference in rates of reactions of eq 3 and 4 is due to a kinetic isotope effect or to a difference in reaction pathway, although preliminary experiments are supportive of the former. Consistent with this interpretation, decarboxylation of the analogous *trans*-$PtH(O_2CH)(PEt_3)_2$ derivative affords the stable $PtH_2(PEt_3)_2$ species plus carbon dioxide.[15] Detailed kinetic and mechanistic investigations addressing this issue are in progress.

Despite the complex nature of the reaction of **1** with CO_2, the analogous $HNi(Ph)(PCy_3)_2$ species undergoes simple CO_2 insertion into the Ni–H bond to quantitatively yield $HCO_2Ni(Ph)(PCy_3)_2$. This is an important observation in that Pd(II) phosphine complexes, known to react with benzene to provide H–Pd–Ph species,[16] have been reported to catalyze the production of benzoic acid from benzene and carbon dioxide.[17] Common proposed cycles for this process include either a phenylmetallocarboxylic acid, HOOC–Pd–Ph, or a hydridometalbenzoate, H–Pd–O_2CPh, as proposed intermediates. The contrasting results of the above nickel study are, in fact, more consistent with literature precedents and suggest that alternate pathways might be available for the Pd-catalyzed carboxylic acid synthesis.

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Supplementary Material Available: A listing of rate data and plots of H/D exchange in $DNi(O_2CH)(Cy_3P)_2$ (2 pages). Ordering information is given on any current masthead page.

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(12) Formic acid is eliminated from **2** upon addition of the oxidative exchange reagent, (*p*-TolS)$_2$, yielding $[(PCy_3)Ni(S\text{-}p\text{-}Tol)_2]_2$. Darensbourg, M. Y.; Ludvig, M., unpublished results.

(13) $[Ni(PCy_3)_2]_2N_2$ (1.54 g) dissolved in 25 mL of toluene was purged with argon until the solution turned yellow in color. The volume was reduced to approximately 7 mL followed by addition of a preequilibrated solution of 0.22 mL D_2O/0.092 mL HCO_2H in 15 mL of Et_2O. The resulting yellow product was isolated by filtration and dried in vacuo (1.40 g, 87% yield). ^{2}H NMR: −27.51 ppm (t), J_{PH} = 11.09 Hz. ^{1}H NMR: 8.91 ppm.

(14) The instability of the dihydride was noted earlier from attempts to prepare $(Cy_3P)_2Ni(Et)H$.[4] In that work H_2 evolved, presumably via β-elimination of the desired complex, yielding $(C_2H_4)Ni(PCy_3)_2$. Nevertheless, in the cold and in the absence of a displacing ligand, the $(Cy_3P)_2Ni(H)_2$ complex might have an appreciable lifetime.

(15) Paonessa, R. S.; Trogler, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 3529.

(16) (a) Fujiwara, Y.; Kawauchi, T.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* **1980**, 220. (b) Fujiwara, Y.; Kawata, I.; Kawauchi, T.; Taniguchi, H. *Ibid.* **1982**, 132.

(17) Sugimoto, H.; Kawata, I.; Taniguchi, H.; Fujiwara, Y. *J. Organomet. Chem.* **1984**, *266*, C44.

Electron Transfer in the Cytochrome *c*/Cytochrome *b*₂ Complex: Evidence for "Conformational Gating"

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Since long distance electron transfer between proteins controls the flow of biological energy, the factors which control these rates remain a subject of intense continuing interest.[1-3] Over the last few years, research ranging from model systems[4-8] to natural protein complexes has shown that in general, such rates are characterized by a strong (~ exponential) dependence on distance[1,4] and also by a strong dependence on reaction free energy[1-12] as embodied in Marcus theory.[1] Although most theoretical treatments assume that the configurational changes which accompany electron transfer (e.g., solvent repolarization) occur rapidly, this is not universally true.[13-16] In particular, Hoffman

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(1) An excellent discussion of reorganization energy is found in the following: Marcus, R.; Sutin, N. *Biochem. Biophys. Acta* **1985**, *811*, 265–312.

(2) Detailed overviews include the following: (a) Chance, B., et al. *Tunneling in Biological Systems*; Academic: NY, 1978. (b) Guarr, T.; McLendon, G. *Coord. Chem. Rev.* **1985**, *68*, 1–52.

(3) McLendon, G. *Acc. Chem. Res.* **1987**, in press.

(4) Closs, G.; Calcaterra, L.; Green, N.; Penfield, K.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673–3678.

(5) Heiler, D.; McLendon, G.; Ragolskyj, P. *J. Am. Chem. Soc.* **1987**, in press.

(6) An elegant special class of "model systems" is based on proteins which have been modified by redox active metal complexes (e.g. cytochrome *c*-His 33–$Ru(NH_3)_5{}^{3+}$): (a) Winkler, J.; Nocera, D.; Bordignon, E.; Gray, H. B. *J. Am. Chem. Soc.* **1982**, *104*, 5798–5800. (b) Isied, S.; Kuehn, C.; Worosilia, G. *J. Am. Chem. Soc.* **1982**, *104*, 7659.

(7) Mayo, S.; Ellis, W.; Crutchley, R.; Gray, H. B. *Science* (*Washington, D.C.*) **1986**, *233*, 948–952.

(8) Other examples include: (a) Miller, J.; Closs, G.; Calcaterra, L. *J. Am. Chem. Soc.* **1984**, *106*, 3047–3049. (b) Passman, P.; Verhoeven, J.; DeBoerth, J. *Chem. Phys. Lett.* **1978**, *57*, 530. (c) Wasielewski, M.; Niemczyk, M. *J. Am. Chem. Soc.* **1984**, *106*, 5043. (d) Creutz, C.; Kroger, P.; Matsubara, T.; Netzel, T.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 5442.

(9) (a) McLendon, G.; Miller, J. R. *J. Am. Chem. Soc.* **1985**, *107*, 7811. (b) Taylor, K.; McLendon, G. *J. Am. Chem. Soc.*, submitted for publication. (c) E.g., Hazzard, J.; Tollin, G. *Biochemistry* **1987**, in press.

(10) (a) McGourty, J.; Blough, N.; Hoffman, B. *J. Am. Chem. Soc.* **1983**, *105*, 4470–7742. (b) Liang, N.; Pielak, G.; Mauk, A. G.; Smith, M.; Hoffman, B. *Proc. Natl. Acad. Sci.* **1987**, *84*, 1249–1252.

(11) (a) Vanderkooi, J.; Glats, P.; Casadei, J.; Woodrow, G. *Eur. J. Biochem.* **1980**; *110*, 189–196. (b) Thomas, M.; Gervais, M.; Faradon, V.; Valat, P. *Eur. J. Biochem.* **1983**, *135*, 577–581.

(12) (a) capelliere Blandin, C. *Eur. J. Biochem.* **1982**, *128*, 533–542. (b) Capelliere Blandin, C. *Biochemie* **1986**, *68*, 745–755.

(13) Recent theoretical treatments have emphasized that solvent repolarization dynamics may control the overall rate of charge transfer: (a) Calef, D.; Wolynes, P. *J. Chem. Phys.* **1983**, *78*, 470–482. (b) Zusman, L. *Chem. Phys.* **1980**, *49*, 295–304. (c) VanderZwan, G.; Hynes, J. T. *J. Chem. Phys.* **1982**, *76*, 2993–3001.

(14) (a) McGuire, M.; McLendon, G. *J. Phys. Chem.* **1986**, *90*, 2549. (b) Weaver, M.; Gennett, T. *Chem. Phys. Lett.* **1985**, *113*, 213–218. (c) Kosawer, E. *Acc. Chem. Res.* **1982**, *15*, 259–266. (d) Grampp, G. *Z. Phys. Chem.* **1986**, *148*, 53–63.

(15) In independent work we have established the redox potentials of Zn cytochrome *c* and porphyrin cytochrome *c* by cyclic voltammetry $E°_{\mathrm{Zn}c} = 0.85$ $E°_{\mathrm{porph}\ c} = 1.05$ including the triplet state energies $^3(\mathrm{Zn}c) = 1.6_5$ (porph *c*) $= 1.4_5$ gives $E°_{(\mathrm{Zn/Zn^+})} = 0.8_4$ $E°_{(^3\mathrm{porph/porph})^+} = 0.40$. Details of this work will be presented elsewhere (Magner, E.; McLendon, G., submitted for publication).

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