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

$$CF_3COOR + 2H_2 \xrightarrow{[IrH_5P_2]} 2ROH \tag{12}$$

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).

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

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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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

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

$^{13}CO_2$ 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

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

[†] On leave of absence from the University of Malaya, Kuala Lumpur, Malaysia.

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(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]

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(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.

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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.

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

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

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

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, $(p\text{-TolS})_2$, 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.

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

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