trans-$(\eta^2\text{-Ethene})_2\text{Cr(CO)}_4$ (**2a**) is thermally stable not only in the solid state but also in the gas phase,[11] in liquid xenon,[12] and in alkane solution. By contrast, $(\eta^2\text{-ethene})\text{Cr(CO)}_5$ (**1a**) is only moderately stable. Monitoring a **1a**/**2a** mixture in ethene-saturated alkane solution at ambient temperature by infrared spectroscopy we observe that **1a** decomposes gradually with formation of Cr(CO)_6, whereas **2a** survives for an extended period of time. Under CO atmosphere **1a** has vanished within a few minutes, but **2a** is still present after several hours, as long as oxygen is strictly excluded.

The photoreactions of Mo(CO)_6 and W(CO)_6 take essentially the same route as illustrated for Cr(CO)_6; Scheme I, M = Mo, W. The only difference is that the formation of **2c** via **1c** [M = W; $\bar{\nu}$(CO) = 2085.5 (w), 1974 (st), 1955.5 (vst) cm^{-1}] occurs at ambient temperature, and the synthesis of **2b** via **1b** [M = Mo; $\bar{\nu}$(CO) = 2086 (w), 1976 (st), $\simeq$1960 (vst) cm^{-1}] is most conveniently performed at −20 °C. The photochemical generation of these compounds has been reported previously together with their infrared data,[4] but they were considered to be too unstable for isolation. However, we have obtained both of the two *trans*-$(\eta^2\text{-ethene})_2\text{M(CO)}_4$ complexes as colorless crystals: **2b**, mp 70–73 °C, 48% yield; **2c**, mp 130–135 °C, 52% yield. The spectroscopic data (Table I) closely resemble those of **2a**, and consequently the same structure can be assigned.

In all our experiments we see no evidence for the formation of any of the *cis*-$(\eta^2\text{-ethene})_2\text{M(CO)}_4$ complexes **3**, but we have to consider the possibility that such a species could be involved as a short-lived intermediate.[8] In fact, ab initio calculations[13] on L-Mo(CO)_5 and low-temperature matrix experiments with $(\eta^2\text{-olefin})\text{W(CO)}_5$ in alkane glass[14] or solid argon[7] indicate initial photodissociation of cis CO. Nevertheless, we find it remarkable that in the gas-phase experiments[2] with $(\eta^2\text{-ethene})\text{Cr(CO)}_5$ and ethene the cis product **3a** is the only observable $(\eta^2\text{-ethene})_2\text{Cr(CO)}_4$ species, and no trace of the stable trans isomer **2a** was observed. A plausible explanation[15] is that the formation of the latter involves **3a** → **2a** photoisomerization.[16] At ambient temperature in the gas phase (or in alkane solution) this photoisomerization may be outstripped by the thermal decay of **3a**. Cooling will provide sufficient stabilization of **3a**, such that its photochemical rearrangement to **2a** becomes feasible, as it happens in liquid xenon[1] or in alkane solution at −50 °C. In going from Cr to Mo and W the stability of type **3** complexes is expected to increase, and, consequently, cooling would become less essential in order to render the **3** → **2** photorearrangement feasible.

In a control experiment we used $(\eta^4\text{-dimethylbutadiene})\text{Cr(CO)}_4$ (**4**)[17] as a source of the *cis*-Cr(CO)_4 unit.[18] Upon treatment with ethene at ambient temperature in the dark **4** disappears gradually with formation of $(\eta^2\text{-ethene})\text{Cr(CO)}_5$ (**1a**) and Cr(CO)_6 as the only soluble products. Most probably these compounds originate from decomposition of labile *cis*-$(\eta^2\text{-ethene})_2\text{Cr(CO)}_4$ (**3a**). However, no trace of *trans*-$(\eta^2\text{-ethene})_2\text{Cr(CO)}_4$ (**2a**) could be detected, thus providing indirect evidence for the involvement of a second photochemical step, $\mathbf{3a} \xrightarrow{h\nu} \mathbf{2a}$, in the synthesis of the latter.

In conclusion we note that the coordination of two ethene ligands to the Cr(CO)_4 moiety nicely parallels the molybdenum and tungsten analogues: all three metals form stable *trans*-$(\eta^2\text{-ethene})_2\text{M(CO)}_4$ complexes **2**. This and the distinctly lower stability of $(\eta^2\text{-ethene})\text{M(CO)}_5$ **1** and *cis*-$(\eta^2\text{-ethene})_2\text{M(CO)}_4$ **3** species is easily understood in terms of optimum metal → π^* (olefin) back donation.[6,7,19-21] Two olefins in trans orthogonal orientation do not compete for metal (d_π) electron density, owing to their single-faced π-acceptor character. By contrast a CO ligand (with its *two* orthogonal π-acceptor orbitals) situated trans to an olefin will strongly rival, thus weakening the metal–olefin bond.

Acknowledgment. Support of this work by the Alexander von Humboldt-Stiftung through a research fellowship (to S.Ö.) is gratefully acknowledged.

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[11] In the gas-phase IR spectrum of **2a** the intensity of the strong ν(CO) band (1967 cm^{-1}) remains constant over several hours.

[12] The apparent lability of **2a** in liquid xenon[1] was disproven by using a pure sample of the complex: M. Poliakoff, private communication.

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[15] We are grateful to the referees for drawing our attention to this point.

[16] The reverse process, **3a** → **2a** photoisomerization, was observed under low-temperature matrix isolation conditions: Klotzbücher, W. E., private communication.

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Novel Catalytic Chemistry of Iridium Polyhydride Complexes

Alan S. Goldman and Jack Halpern*

Department of Chemistry, The University of Chicago
Chicago, Illinois 60637

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Polyhydride complexes of transition metals ($[\text{MH}_x\text{L}_y]$, where L is a ligand such as a tertiary phosphine), constitute a distinctive class of compounds which have been widely studied in other contexts[1] but whose catalytic chemistry has not thus far been extensively explored. Earlier studies[2,3] have demonstrated the effectiveness of polyhydride complexes, e.g., $[\overline{\text{Ru}}\text{H}_2(\text{PPh}_3)_2(\text{PPh}_2\overline{\text{C}_6}\text{H}_4)]^-$, $[\text{RuH}_3(\text{PPh}_3)_3]^-$, $[\text{RuH}_5(\text{PPh}_3)_2]^-$, and $[\text{RuH}_4(\text{PPh}_3)_3]$, as catalysts or catalyst precursors for the hydrogenation of a variety of substrates including ketones, esters, and arenes which are not readily hydrogenated by most other homogeneous catalysts. Distinctive features of these systems appear to include the ability of such polyhydride complexes to serve as highly loaded "hydrogen reservoirs" and the accessibility of vacant coordination sites through the facile reductive elimination or transfer of coordinated hydrogen.

Extending these studies we now have uncovered significantly different reactivity patterns for the iridium polyhydride complex $[\text{IrH}_5\text{P}_2]$ (P = P-*i*-Pr$_3$)[4] and derivatives thereof, some features of which are unprecedented. We report here preliminary results of these studies.

$[\text{IrH}_5\text{P}_2]$ reacts with the activated ester CF_3COOR (R = CH_2CF_3) in cyclo-C_6D_{12}[5] at 60 °C to yield $[\text{IrH}_2\text{P}_2(\text{OR})]$[6] in

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[1] For leading references, see: (a) Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, 415–452. (b) Caulton, K. G. *Ann. N. Y. Acad. Sci.* **1983**, *415*, 27–36.

[2] (a) Pez, G. P.; Grey, R. A.; Corsi, J. *J. Am. Chem. Soc.* **1981**, *103*, 7528–7535. (b) Grey, R. A.; Pez, G. P.; Wallo, A. *Ibid.* **1980**, *102*, 5548–5549. (c) Grey, R. A.; Pez, G. P.; Wallo, A. *Ibid.* **1981**, *103*, 7536–7542. (d) Grey, R. A.; Pez, G. P.; Wallo, A.; Corsi, J. *J. Chem. Soc., Chem. Commun.* **1980**, 783–784.

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[4] Garlaschelli, L.; Kahn, S. I.; Bau, R.; Longoni, G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1985**, *107*, 7212–7213.

[5] Deuteriated aromatic solvents could not be used in these studies because of facile isotopic exchange with $[\text{IrH}_5\text{P}_2]$.

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accord with eq 1.

$$[IrH_5P_2] + CF_3COOR \rightarrow [IrH_2P_2(OR)] + ROH \quad (1)$$

The reaction was preceded by an induction period (ca. 1 h) which, however, was not observed when some $[IrH_2P_2(OR)]$ was added initially to the solution. Kinetic measurements[8] encompassing the initial concentration ranges, 3.3×10^{-3}–1.2×10^{-2} M $[IrH_5P_2]$, 2.0×10^{-2}–1.0×10^{-1} M $[IrH_2P_2(OR)]$, 6.0×10^{-2}–4.0×10^{-1} M CF_3COOR, and 2.6×10^{-3}–4.1×10^{-2} M ROH, yielded the rate law, eq 2, with $k_2 = 1.25 \times 10^{-4}$ $M^{-1/2}$ s^{-1} at 60 °C.

$$-d[IrH_5P_2]/dt = k_2[IrH_5P_2]^{1/2}[IrH_2P_2(OR)]^{1/2}[CF_3COOR][ROH]^{-1/2} \quad (2)$$

Under pseudo-half-order conditions ($[IrH_2P_2(OR)]$, CF_3COOR, and ROH in excess), the rate law reduces to

$$-d[IrH_5P_2]/dt = k_{obsd}[IrH_5P_2]^{1/2} \quad (3)$$

$$k_{obsd} = k_2[IrH_2P_2(OR)]^{1/2}[CF_3COOR][ROH]^{-1/2} \quad (4)$$

Supporting kinetic data are reported in Figure 1.

This kinetic behavior can be accommodated by the following mechanistic scheme, according to which $k_2 = (K_5^{eq})^{1/2}k_6$.

$$[IrH_5P_2] + [IrH_2P_2(OR)] \xrightleftharpoons[\text{rapid equilibrium}]{K_5^{eq}} 2[IrH_3P_2] + ROH \quad (5)$$

$$[IrH_3P_2] + CF_3COOR \xrightarrow[\text{rate determining}]{k_6} [IrH_2P_2\{OCH(OR)CF_3\}] \xrightarrow{\text{fast}} [IrH_2P_2(OR)] + CF_3CHO \quad (6)$$

$$[IrH_3P_2] + CF_3CHO \xrightarrow{\text{fast}} [IrH_2P_2(OR)] \quad (7)$$

Support for the proposed role of $[IrH_2P_2(OR)]$ as an "H_2 sponge" (eq 5) is provided by our finding that addition of ca. 5×10^{-3} M of another efficient H_2 acceptor, $[IrI(CO)(PPh_3)_2]$,[9] in place of $[IrH_2P_2(OR)]$, also resulted in elimination of the induction period of reaction 1, presumably by generating $[IrH_3P_2]$ through the reaction[10]

$$[IrH_5P_2] + [IrI(CO)(PPh_3)_2] \rightleftharpoons [IrH_3P_2] + [IrH_2I(CO)(PPh_3)_2] \quad (8)$$

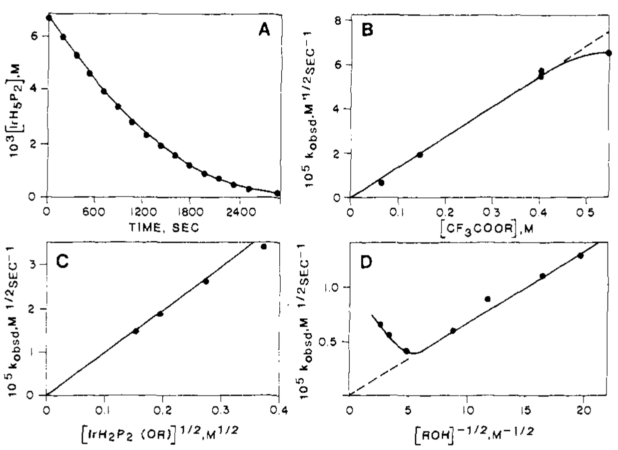

Figure 1. Kinetics of reaction 1 in C_6D_{12} at 60 °C. (A) Pseudo-half-order rate plot for reaction of 6.9×10^{-3} M $[IrH_5P_2]$ with 0.40 M CF_3COOR in solution containing initially 0.039 M $[IrH_2P_2(OR)]$ and 0.065 ROH. Circles are experimental data points; curve is best fit half-order plot calculated according to eq 3. (B) Dependence of k_{obsd} on $[CF_3COOR]$ (initial concentrations: 3.2×10^{-2} M $[IrH_2P_2(OR)]$; 1.2×10^{-2} M $[IrH_5P_2]$; 6.5×10^{-2} M ROH). (C) Dependence of k_{obsd} on $[IrH_2P_2(OR)]$ (initial concentrations: 0.136 M CF_3COOR; 6.5×10^{-2} M ROH). (D) Dependence of k_{obsd} on initial [ROH] (initial concentrations: 5×10^{-3} M $[IrH_5P_2]$; 0.04 M CF_3COOR; 1.84×10^{-2} M $[IrH_2P_2(OR)]$). (For experiments at low initial ROH concentrations, k_{obsd} was deduced from *initial* rate measurements so that the $[IrH_2P_2(OR)]$ and ROH concentrations were effectively constant.)

Departures from the rate law of eq 2 were observed outside the concentration ranges specified above, notably the following.

(i) Above 0.4 M CF_3COOR, the rate tended to level off with further increase in the CF_3COOR concentration (Figure 1B). This is attributable to reaction 5 becoming rate-limited by reductive elimination of H_2 according to the scheme of eq 9. The rate constant of the H_2 loss step (k_{10}) was determined independently to be $(4.9 \pm 0.4) \times 10^{-3}$ s^{-1} at 60 °C by measuring the kinetics of the replacement reaction 10. The limiting rate of reaction 1 at low ROH concentrations ($<2.0 \times 10^{-3}$ M) also was found to agree with the rate of loss of H_2 (k_{10}).

$$[IrH_5P_2] \xrightleftharpoons{-[IrH_3P_2]} H_2 \xrightleftharpoons{[IrH_2P_2(OR)]} [IrH_3P_2] + ROH \quad (9)$$

$$[IrH_5P_2] \xrightleftharpoons[H_2(k_{-10})]{-H_2(k_{10})} [IrH_3P_2] \xrightarrow[k_{11}]{P(OMe)_3} [IrH_3P_2\{P(OMe)_3\}] \quad (10)$$

(ii) Above 0.04 M ROH the rate *increases* with increasing ROH concentration (Figure 1D). This is attributable to a medium effect, and, consistent with this, it was found that addition of an inert polar solvent, 2,2,5,5-tetramethyltetrahydrofuran, also increased the reaction rate.

$[IrH_2P_2(OR)]$ was found to react immediately with H_2 (1 atm, 25 °C) to regenerate $[IrH_5P_2]$ (eq 11).

$$[IrH_2P_2(OR)] + 2H_2 \rightarrow [IrH_5P_2] + ROH \quad (11)$$

The combination of eq 1 and eq 11 constitutes a catalytic cycle for the hydrogenation of CF_3COOR (eq 12). However, no reaction of CF_3COOR (0.16 M) with H_2 (1 atm) occurred in a C_6D_{12} solution containing 1.5×10^{-2} M $[IrH_5P_2]$ (80 h at 80 °C). This is attributable to suppression by H_2 of accumulation of the

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(6) $[IrH_2P_2(OR)]$ was synthesized independently by the reaction, $[IrH_5P_2] + 2CH_2{=}CHC(CH_3)_3 + ROH \rightarrow [IrH_2P_2(OR)] + 2CH_3CH_2C(CH_3)_3$ and characterized by satisfactory elemental analysis [calcd (found): C, 39.14 (39.00); H, 7.55 (7.42); F, 9.29 (9.37); P, 10.09 (9.85)], molecular weight determination [(1.03 ± 0.1) × calculated mw of monomer] and spectroscopically [NMR (C_6D_{12}, 28 °C) ^1H δ −31.2 (2 H, t, $^3J_{P-H} = 13.5$ Hz, IrH), 1.23 (36 H, pseudo-quartet, $((^5J_{P-H} + {}^3J_{P-H})/2 = 6.6$ Hz, $^3J_{H-H} = 7.0$ Hz, $PCH(CH_3)_2$), 2.23 (6 H, m, $^4J_{P-H} \sim {}^2J_{P-H} \sim 3.5$ Hz, $^3J_{H-H} = 7.0$ Hz, $PCH(CH_3)_2$), 4.38 (2 H, q, $^3J_{F-H} = 9.3$ Hz, OCH_2CF_3); ^{31}P (selectively decoupled from aliphatic proton region) δ 51.0 (t, J_{H-P} (apparent) ≈ 13 Hz); ^{19}F δ −78.1 (t, $^3J_{H-F} = 9.3$ Hz)]. The NMR spectrum is consistent with a trans P_2 trigonal bipyramidal structure similar to the structures previously assigned to the analogous $[IrH_2(PR_3)_2Cl]$ complexes (R = *i*-Pr, *t*-Bu, cyclohexyl).[7] As with the latter compounds, the corresponding carbonyl derivative *cis*-,*trans*-$[IrH_2P_2(OR)(CO)]$ was obtained by reacting $[IrH_2P_2(OR)]$ with CO. The ^1H and ^{31}P spectra of $[IrH_2P_2(OR)(^{13}CO)]$ confirm this configuration. $[IrH_2P_2(OR)]$ exchanges rapidly with free ROH on the ^1H and ^{19}F NMR time scale.

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(8) The rate was measured by monitoring the disappearance of $[IrH_5P_2]$ by ^1H NMR.

(9) (a) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3511–3514. (b) Vaska, L.; Werneke, M. F. *Trans. N. Y. Acad. Sci.* **1971**, *33*, 70–86.

(10) Although the equilibria of eq 5 and 9 lie far to the left, it proved possible to trap labile N_2 adducts of "IrH_3P_2" at low temperatures. Passing H_2 into a toluene-d_8 solution of $[IrH_2P_2(OR)]$ under N_2 at −40 °C yielded (together with ROH) a mixture (variable ratio depending on the N_2 concentration) of two species, $[(IrH_3P_2)]_n(N_2)]$, $n = 1$ or 2, presumably through the reaction sequence, $[IrH_2P_2(OR)] + H_2 \rightleftharpoons [IrH_3P_2] + ROH$; $[IrH_3P_2] + N_2 \rightleftharpoons [IrH_3P_2(N_2)]$; $[IrH_3P_2(N_2)] + [IrH_3P_2] \rightleftharpoons [(IrH_3P_2)_2(N_2)]$. The ^1H and ^{31}P NMR spectra of the N_2 complexes and their $^{15}N_2$ analogues were fully consistent with trans P_2 configurations. Treatment with CO resulted in facile displacement of N_2 and formation of the corresponding stable CO adduct, $[IrH_3P_2(CO)]$.[11] Warming the N_2 complexes in the presence of ROH resulted in formation of equimolar amounts of $[IrH_5P_2]$ and $[IrH_2P_2(OR)]$, in accord with $^2/_n[(IrH_3P_2)_n(N_2)]$ ($n = 1$ or 2) + ROH $\rightarrow [IrH_5P_2] + [IrH_2P_2(OR)] + {}^2/_nN_2$.

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

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

While the behavior cited above would appear to limit the utility of $[\mathrm{IrH_5P_2}]$ 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 $[\mathrm{IrH_5P_2}]$, indeed, is a very efficient catalyst or catalyst precursor for the transfer hydrogenation of *tert*-butylethylene by isopropyl alcohol (eq 13).

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

At 30 °C, with initial concentrations of 0.12 M $\mathrm{CH_2{=}CHC(CH_3)_3}$, 0.60 M $\mathrm{(CH_3)_2CHOH}$, and 5.0×10^{-3} M $[\mathrm{IrH_5P_2}]$, reaction 13 exhibited autocatalytic kinetics and was essentially complete in ca. 50 min. Initial addition of 0.2 M $\mathrm{(CH_3)_2C{=}O}$ 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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[13] At much higher temperatures (100–150 °C), $[\mathrm{IrH_5P_2}]$ 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]

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The Reaction of $(\mathrm{Cy_3P})_2\mathrm{Ni(H)(CH_3)}$ with Carbon Dioxide. Formation of a Hydridonickel Formate Complex, $\mathrm{HNi(O_2CH)(Cy_3P)_2}$

Donald J. Darensbourg,* Marcetta Y. Darensbourg,*
Lai Yoong Goh,[†] Maria Ludvig, and Philip Wiegreffe

Department of Chemistry, Texas A&M University
College Station, Texas 77843

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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 ($\mathrm{PCy_3}$). First synthesized by Jonas and Wilke, *trans*-$(\mathrm{Cy_3P})_2\mathrm{Ni(H)(CH_3)}$, **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

$$\underset{\mathbf{1}}{(\mathrm{Cy_3P})_2\mathrm{Ni(H)(CH_3)}} + \mathrm{CO_2} \xrightarrow{-50\ ^\circ\mathrm{C}} \underset{\mathbf{2}}{(\mathrm{Cy_3P})_2\mathrm{Ni(H)(O_2CH)}} + \mathrm{CH_4} + \mathrm{C_2H_6} + \ldots \qquad (1)$$

$^{13}\mathrm{CO_2}$ the reaction was readily monitored by $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR. At −50 °C the major metal-containing product (ca. 35%) detected was *trans*-$(\mathrm{Cy_3P})_2\mathrm{Ni(H)(O_2CH)}$, **2**, which was separated by chromatography on a silica gel column and recrystallized several times from hexane/THF. Product **2** was identified by ^{1}H, ^{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 $\mathrm{HCO_2H}$ to $\{(\mathrm{Cy_3P})_2\mathrm{Ni}\}_2\mathrm{N_2}$ analogous to the synthesis of $(\mathrm{Cy_3P})_2\mathrm{Ni(H)(OAc)}$.[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 $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum and a ^{1}H 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 $(\mathrm{Cy_3P})_2\mathrm{Ni(CH_3)O_2CH}$. Further support for this suggestion is provided by the reaction of the phenyl analog of **1**, $(\mathrm{Cy_3P})_2\mathrm{Ni(H)(Ph)}$, **3**, with carbon dioxide yielding $(\mathrm{Cy_3P})_2\mathrm{Ni(Ph)(O_2CH)}$ (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 ^{1}H NMR and supported by elemental analysis, this product is formulated as the dimer $\mathrm{(CH_3)(Cy_3P)Ni(O_2CO)Ni(H)(PCy_3)_2}$,[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 $^2\mathrm{H}\{^1\mathrm{H}\}$ NMR, eq 2. Furthermore, no ethylene or

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

[†] 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: ^{1}H NMR ($\mathrm{C_6D_6}$, 23 °C) δ 8.90 (s, Ni–$\mathrm{O_2CH}$), δ −27.59 (t, Ni–H, $J_{\mathrm{H-P}} = 77$ Hz); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 23 °C) δ 166.7 (s, Ni–$\mathrm{CO_2H}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 23 °C) δ 33.47 (d, $J_{\mathrm{C-P}} = 67.9$ Hz, $\mathrm{PCy_3}$); IR (KBr cell) CO_2 adsorption at 1619 and 1310 cm^{-1}, $\nu_{\mathrm{Ni-H}}$ at 1931 cm^{-1}. Anal. Calcd for $\mathrm{C_{37}H_{68}O_2P_2Ni}$: 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*-$\mathrm{PtH(O_2CH)[P(C_6H_{11})_3]_2}$, 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% $\mathrm{C_{56}H_{103}O_3P_3Ni_2}$ and 20% $\mathrm{C_{37}H_{68}O_2P_2Ni}$: 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**: ^{1}H NMR ($\mathrm{C_6D_6}$, 23 °C) δ −0.47 (d, $J_{\mathrm{H-P}} = 4.1$ Hz, Ni–$\mathrm{CH_3}$), δ −28.45 (t, $J_{\mathrm{H-P}} = 76.5$ Hz, Ni–H); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 23 °C) δ 170.6 (s, Ni–$\mathrm{O_2CO}$–Ni); $^{13}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6H_6}$, 23 °C) δ 44.0 (s, Ni–$\mathrm{P_a}$), δ 32.5 (d, $J_{\mathrm{P-C}} = 68.5$ Hz, Ni–$\mathrm{P_b}$); 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 $\mathrm{(CH_2CMe_2Ph)(PMe_3)Ni(O_2CO)Ni(CH_2CMe_2Ph)(PMe_3)_2}$(IR (Nujol mull) $\mathrm{CO_3}$ at 1505 cm^{-1}; $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 21 °C) δ 170.4 (s, $\mathrm{CO_3}$)) 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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