Further studies of this interesting reaction are in progress.[14]

Registry No. I, 82190-58-7; II, 82182-23-8; IIIb, 82823-96-9; IVa, 82823-97-0; IVb, 82823-98-1; $TaCl_5$, 7721-01-9; LiOAr′, 55894-67-2; $LiCH_3$, 917-54-4; LiPh, 591-51-5.

Supplementary Material Available: Tables of bond angles, bond distances, fractional coordinates and isotropic thermal parameters, and anisotropic thermal parameters for IIIb (11 pages). Ordering information is given on any current masthead page.

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(14) We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support.

Ancillary Ligand Rearrangements Promoted by the Migratory Insertion of Carbon Monoxide into Nickel(II)–Carbon Bonds

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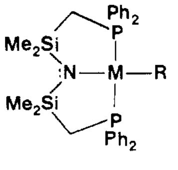
Summary: Migratory insertion of CO into the nickel(II) carbon bonds of $[Ni(R)N(SiMe_2CH_2PPh_2)_2]$ promotes a rearrangement of the amidophosphine hybrid ligand to generate a nickel(0) dicarbonyl derivative, $[Ni(CO)_2\{RCON(SiMe_2CH_2PPh_2)_2\}]$. With the palladium–methyl derivative $[Pd(CH_3)N(SiMe_2CH_2PPh_2)_2]$, only the palladium(II) acetyl complex $[Pd(COCH_3)N(SiMe_2CH_2PPh_2)_2]$ is formed with no evidence of anicillary ligand rearrangement.

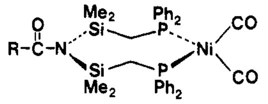
Our approach to fine-tuning the reactivity patterns of a given transition-metal complex involves the use of ancillary multidentate ligands that contain vastly different donor atom types. Up to the present we have investigated the coordination chemistry of bidentate and tridentate "hybrid" ligands containing the *hard* amido donor NR_2^- (R = alkyl or silyl) and *soft* phosphine donors with a number of different transition metals.[1,2] The primary purpose of these "hybrid" ligands is to provide new electronic and steric environments for a given metal while being inert to further transformations at the metal center; however, we have found that in certain cases, notably nickel(II), this type of ligand system is noninnocent and undergoes a dramatic rearrangement.

We have previously reported[1b] the synthesis of organonickel and organopalladium derivatives (1) containing the uninegative, tridentate ligand $N(SiMe_2CH_2PPh_2)_2$. All of the organonickel complexes (**1a–d**) react[3] with carbon monoxide at atmospheric pressure to form new products that involve a change in formal oxidation state of the metal as well as a change in the chelating mode of the "hybrid" ligand.



1a, M = Ni, R = CH_3
b, M = Ni, R = η^3-C_3H_5
c, M = Ni, R = $CH{=}CH_2$
d, M = Ni, R = C_6H_5
e, M = Pd, R = CH_3

When gold-orange solutions of the nickel–methyl complex **1a** are exposed to CO under ambient conditions, the color fades over a period of 5 min to produce a new, single compound (**2a**) in quantitative yield (by ^1H NMR spectroscopy) with the overall uptake of 3 equiv of CO. *Colorless* crystals of **2a** can be isolated in 90% yield; analytical and solution molecular weight data are consistent with the monomeric empirical formula $[Ni(CH_3)N(SiMe_2CH_2PPh_2)_2(CO)_3]$.[4] The solution infrared spectrum of **2a** consists of two very strong terminal carbonyl bands at 1995 and 1930 cm^{-1} (which shift to 1955 and 1890 cm^{-1} with ^{13}CO) and a strong band at 1715 cm^{-1} (which shifts to 1680 cm^{-1} with ^{13}CO). **2a** is formulated as a nickel(0) dicarbonyl derivative wherein the ligand binds in a bidentate mode through the phosphine donors because of the formation of an *N*-acetyl group. Consistent with this proposal are the $^{13}C\{^1H\}$ NMR data that have a singlet at 161.9 ppm for the amide carbonyl carbon (Si_2NCOCH_3) and a triplet ($^2J_{^{31}P-^{13}C}$ = 2.4 Hz) for the terminal carbonyl ligands at 200.2 ppm. An identical reaction obtains for the allylnickel derivative **1b** to give **2b** as the only observed product,[5] once again as colorless crystals in 80% recrystallized yield. The key evidence for this type of structure is the acyl band in the IR spectrum at 1715 cm^{-1} which indicates an *amide*-type carbonyl rather than a nickel–acyl species.



2a, R = CH_3
b, R = $CH_2CH{=}CH_2$
c, R = $CH{=}CH_2$
d, R = C_6H_5

To test the generality of this reaction, the migratory insertion behavior of the sp^2-carbon ligands, vinyl ($CH{=}CH_2$) and phenyl (C_6H_5), was investigated.[6] The analogous reaction of CO with the vinylnickel complex **1c** proceeds

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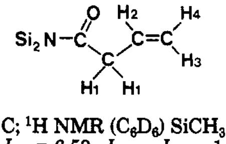
(1) (a) Fryzuk, M. D.; MacNeil, P. A. *J. Am. Chem. Soc.* **1981,** *103,* 3592. (b) Fryzuk, M. D.; MacNeil, P. A., Rettig, S. J.; Secco, A. S.; Trotter, J. *Organometallics* **1982,** *1,* 918.

(2) Fryzuk, M. D.; Williams, H. D.; Rettig, S. J., submitted for publication in *Inorg. Chem.* Zirconium and hafnium complexes of hybrid multidentate ligands are described.

(3) All reactions with CO and ^{13}CO (90% ^{13}C) were performed at 1 atm of pressure at room temperature in dry toluene. Typically, ~0.2 mol L^{-1} solutions of the nickel complexes 1 were rapidly stirred under carbon monoxide for the indicated times. The toluene was removed under vacuum and the residue recrystallized from hexanes at −30 °C.

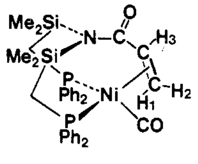
(4) **2a**: mp 122 °C; mol wt (Signer), theoretical 689 found, 698; ^1H NMR (C_6D_6) $SiCH_3$, δ −0.11 (s), CH_2P, 1.89 (br d), $COCH_3$, 1.91 (s), $P(C_6H_5)$, 6.95 (m, para/meta), 7.53 (m, ortho). Anal. Calcd for $C_{34}H_{39}NNiO_3P_2Si_2$: C, 59.48; H, 5.68; N, 2.04. Found: C, 59.30; H, 5.73; N, 1.80.



(5) **2b**: mp 138–140 °C; ^1H NMR (C_6D_6) $SiCH_3$, δ −0.10 (s), CH_2P, 1.84 (br dd), H_1, 3.08 (dt, 2, $J_{1,2}$ = 6.59, $J_{1,3}$ = $J_{1,4}$ = 1.46 Hz), H_2, 5.85 (m, 1, $J_{2,4}$ = 10.01, $J_{2,3}$ = 17.09 Hz), H_3, 5.02 (m, 1, $J_{3,4}$ = 1.71 Hz), H_4, 4.85 (m, 1), $P(C_6H_5)$, 6.95 (m, para/meta), 7.52 (m, ortho). Anal. Calcd for $C_{36}H_{41}NNiO_3P_2Si_2$: C, 60.67; H, 5.76; N, 1.97. Found: C, 60.66; H, 5.89; N, 1.80.

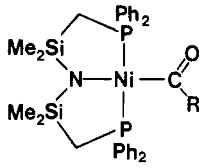
(6) Although migratory insertion of CO into nickel–carbon bonds is well-known, the relative migratory aptitudes of alkyl, aryl, and vinyl derivatives of nickel have not yet been established. See, for example: (a) Klein, H. F.; Karsch, H. H. *Chem. Ber.* **1976,** *109,* 2524. (b) Stroppioni, P.; Dapporto, P.; Sacconi, L. *Inorg. Chem.* **1978,** *17,* 718. (c) Carmona, E.; Gonzalez, F.; Poveda, M. L.; Atwood, J. L.; Rogers, R. L. *J. Chem. Soc., Dalton Trans.* **1980,** 2108. (d) Tremont, S. J.; Bergman, R. G. *J. Organomet. Chem.* **1977,** *140,* C12.

more slowly than that of **1a** or **1b** to give, after 3 h, a mixture of two identifiable products. The rearranged Ni(0) derivative **2c** is obtained as the major product[7] in ~90% yield (by ^{1}H NMR spectroscopy) as well as another Ni(0) derivative, **3**; this latter complex[8] can be separated and obtained pure as yellow microcrystals by careful, repeated recrystallizations from hexane. **3** is formulated as an η^2-acryloyl complex wherein the rearranged ligand binds in a novel tridentate fashion. Consistent with this proposed structure for **3** are the ^{1}H NMR data[8] that show four resonances for the diastereotopic silyl methyl groups due to the chirality of the coordinated acryloyl ligand. In addition, the resonances of the coordinated olefin are shifted upfield and are split by two inequivalent phosphorus nuclei. The infrared spectrum has only one very strong terminal carbonyl stretch at 1950 cm^{-1} as well as a strong band at 1625 cm^{-1} ascribed to ν_{CO} of the η^2-acryloyl function. Additional support for this formulation comes from the ^{31}P{^{1}H} NMR spectrum which consists of an AX doublet of doublets (δ_A 16.38, $\delta_X = -1.38$, $J_{AX} = 57.9$ Hz) for the inequivalent phosphines.



3

The phenylnickel derivative **1d** also produces a mixture of compounds in its reaction with carbon monoxide; after 7 h at ambient conditions, the Ni(0) derivative,[9] **2d**, and the nickel–benzoyl complex,[10] **4d**, were obtained as an approximately 1:1 mixture in quantitative yield (by ^{1}H NMR spectroscopy). Predictably, no product due to coordination of the *N*-benzoyl fragment, analogous to **3**, is observed. Identification of these products was made possible by a Pasteur-type separation of the colorless crystals of **2d** from the orange prisms of **4d**. As anticipated, the reaction of pure **4d** with additional CO resulted in the formation of the *N*-benzoylnickel(0) species, **2d**. If the reaction of the phenylnickel complex **1d** with CO is monitored by ^{1}H NMR spectroscopy, the nickel(II) benzoyl derivative **4d** is formed rapidly and quantitatively at room temperature (<30 min); however, the subsequent reaction to form **2d** is much slower, going to completion in approximately 2 days.



4a, R = CH_3
b, R = $CH_2CH{=}CH_2$
c, R = $CH{=}CH_2$
d, R = C_6H_5

The palladium–methyl analogue, **1e**, does not measurably react with atmospheric pressures of CO, even after 3 days. However, higher pressures (20 atm) generate quantitative yields (^{1}H NMR spectroscopy) of the palladium acetyl complex, $[Pd(COCH_3)N(SiMe_2CH_2PPh_2)_2]$;[11] further reaction with CO was not observed. Indeed, no other transition metal incorporating this ligand system[12] rearranges like that of the nickel derivatives with CO.

The mechanism for this fascinating rearrangement must involve initial formation of the acylnickel species **4** followed by, in a subsequent step, reductive elimination of the nickel(II) amide acyl to give the nickel(0) products. By monitoring[13] the reaction of **1a** or **1b** with carbon monoxide at −40 °C by either ^{31}P{^{1}H} or ^{1}H NMR spectroscopy, we observe very straightforward conversions, via the acyl species **4a** and **4b**, to the nickel(0) products **2a** and **2b**. We are at present investigating the kinetics of this rearrangement and the effect of other ligands on this process.

Acknowledgment. Financial support for this research was generously provided by the Department of Chemistry, the Natural, Applied and Health Sciences Fund (UBC), and the Natural Sciences and Engineering Research Council of Canada. P.A.M. thanks the Walter C. Sumner Foundation for a Memorial Fellowship.

Registry No. 1a, 81603-07-8; **1b**, 82865-00-7; **1c**, 81610-99-3; **1d**, 81603-09-0; **1e**, 81603-11-4; **2a**, 82865-01-8; **2b**, 82865-02-9; **2c**, 82865-03-0; **2d**, 82865-04-1; **3**, 82865-05-2; **4a**, 82865-06-3; **4b**, 82865-07-4; **4d**, 82865-08-5; CO, 630-08-0.

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[7] Although **2c** is the major product, it has not yet been obtained analytically pure due to contamination by **3**. **2c**: ^{1}H NMR (C_6D_6) $SiCH_3$, δ −0.08 (s), CH_2P, 1.85 (br s), H_1, 6.17 (dd, $J_{1,3} = 17.0$, $J_{1,2} = 2.0$ Hz), H_2, 5.38 (dd, $J_{2,3} = 10.2$ Hz), H_3, 5.99 (dd), $P(C_6H_5)$, 6.95 (m, para/meta), 7.15 (m, ortho); IR (CH_2Cl_2, cm^{-1}) ν_{CO}, 1966 (s), 1935 (s), $\nu_{COCH{=}CH_2}$, 1700 (m).

[8] **3**: ^{1}H NMR (C_6D_6) $SiCH_3$, δ 0.65 (d, $^4J_{H,P} = 0.98$ Hz), 0.35 (d, $^4J_{H,P} = 0.98$ Hz), −0.35 (s), −0.65 (s), CH_2P, 1.22 (m), H_1, 4.34 (m, $J_{1,3} = 11.72$, $J_{1,P1} = 6.59$, $J_{1,P2} = 1.46$ Hz), H_2, 3.89 (m, $J_{2,3} = 7.57$, $J_{2,P1} = 5.62$, $J_{2,P2} = 4.15$ Hz), H_3, 4.14 (m, $J_{3,P1} = 13.92$, $J_{3,P2} = 3.17$ Hz), $P(C_6H_5)$, 6.70, 6.98 (m, para/meta), 7.48, 7.92 (m, ortho). Anal. Calcd for $C_{34}H_{39}NNiO_2P_2Si_2$: C, 60.89; H, 5.82; N, 2.09. Found: C, 60.86; H, 6.00; N, 1.82. This type of π complex with α,β-unsaturated amides is known; see: Yamamoto, T.; Igarashi, K.; Komiya, S.; Yamamoto, A. *J. Am. Chem. Soc.* **1980**, *102*, 7448.

[9] **2d**: ^{1}H NMR (C_6D_6) δ $SiCH_3$, δ −0.03 (s), CH_2P, 1.93 (br s), $P(C_6H_5)$ and COC_6H_5, 6.92 (m), 7.52 (m); IR (CH_2Cl_2, cm^{-1}) ν_{CO} 2000 (s), 1935 (s), ν_{COPh} 1680 (m). Anal. Calcd for $C_{39}H_{41}NNiO_3P_2Si_2$: C, 62.57; H, 5.48; N, 1.87. Found: C, 63.00; H, 5.73; N, 1.65.

[10] **4d**: ^{1}H NMR (C_6D_6) $SiCH_3$, δ −0.01 (s), 0.45 (s), PCH_2, 1.54 (dt, $J_{gem} = 13.7$, $J_{app} = 6.5$ Hz), 1.80 ($J_{app} = 5.0$ Hz), $P(C_6H_5)_2$ and COC_6H_5, 6.75 (m), 7.12 (m), 7.28 (m), 7.90 (m), 8.21 (m); IR (KBr, cm^{-1}) ν_{NiCOPh} 1602 (m). Anal. Calcd for $C_{37}H_{41}NNiOP_2Si_2$: C, 64.16; H, 5.92; N, 2.02. Found: C, 64.31; H, 5.98; N, 2.16. The proton NMR data are consistent with restricted rotation of the NiCOPh group about the Ni–C bond, presumably due to the interaction of the nickle–benzoyl moiety with the phenyl substituents on the phosphorus donors. Heating **4d** to >70 °C causes broadening and coalescence of the proton NMR resonances (and some formation of the starting nickel–phenyl complex **1d**).

[11] $[Pd(COCH_3)N(SiMe_2CH_2PPh_2)_2]$: mp 153 °C; ^{1}H NMR ($C_6D_6$) $SiCH_3$, δ 0.24 (s), CH_2P, 1.75 (t, $J_{app} = 6.25$), $COCH_3$, 1.64 (t, $^4J_{H,P} = 2.20$ Hz), $P(C_6H_5)$, 7.02 (m, para/meta), 7.74 (m, ortho); IR (CH_2Cl_2, cm^{-1}) ν_{COCH_3} 1640 (m). Anal. Calcd for $C_{32}H_{39}NOP_2PdSi_2$: C, 56.72; H, 5.76; N, 2.07. Found: C, 57.03; H, 5.64; N, 2.41.

[12] Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J., manuscript in preparation. Rhodium and iridium complexes of hybrid multidentate ligands are described.

[13] The acyl derivatives **4a** and **4b** can be prepared in situ by shaking an NMR tube of the nickel–alkyl derivatives **1a** or **1b** under 1 atm of CO at −78 °C for 5–10 min; the tube was then sealed under CO with a torch. At −40 °C the conversion of **4a** to **2a** has a half-life of ~30 min. **4a**: ^{1}H NMR (C_7D_8, −80 °C) $SiCH_3$, δ 0.16 (br s), 0.63 (br s), CH_2P, 1.19 (br m), $COCH_3$, 1.41 (br t, $^{13}COCH_3$, $^2J_{^{13}C} = 4.5$ Hz), $P(C_6H_5)$, 6.81 (br m, para/meta), 8.34 (br m, ortho); ^{31}P {^{1}H} (C_7D_8, −40 °C, relative to external $P(OMe)_3$ at 141.0 ppm) 27.8 ppm (s). As with **4d**,[10] the ^{1}H NMR is consistent with restricted rotation of the $NiCOCH_3$ group about the Ni–C bond at low temperatures.

Oxidative Conversion to a Terminal Carbene Ligand of a Bridging Carbene in a Dinuclear Iron–Cobalt Complex

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Summary: We report the synthesis of a new carbene-bridged dinuclear complex, $Cp(CO)Fe(\mu\text{-}CO)[\mu\text{-}C(SMe)_2]$-