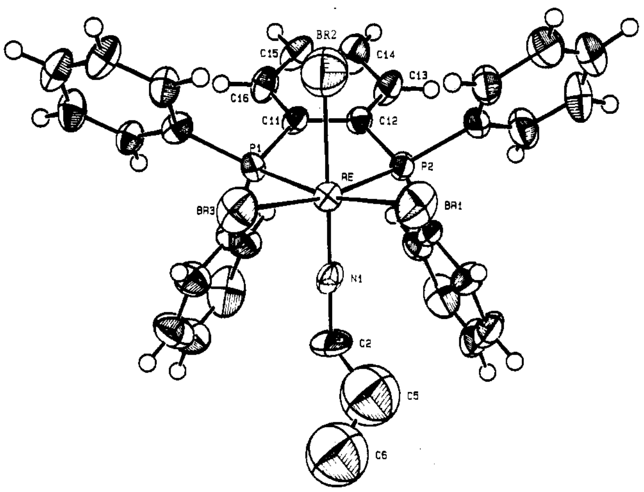

Figure 1. ORTEP view of the structure of Re(N-*n*-Pr)Br_3(dppbe). The thermal ellipsoids are drawn at the 50% probability level. This view represents half of the disorder associated with the CH_2CH_3 fragment of the *n*-propylimido ligand. Atoms C(5) and C(6) have counterparts C(3) and C(4) in the other half of the disorder. Important bond lengths (Å) and angles (deg) are as follows: Re–Br(1) = 2.551 (1), Re–Br(2) = 2.525 (2), Re–Br(3) = 2.563 (1), Re–P(1) = 2.411(3), Re–P(2) = 2.415 (3), Re–N(1) = 1.719 (8), N(1)–C(2) = 1.41 (1), Br(2)–Re–N(1) = 171.2 (2), Br(1)–Re–P(1) = 168.32 (7), Br(3)–Re–P(2) = 169.96 (7), Br(1)–Re–Br(3) = 86.88 (4), Re–N(1)–C(2) = 178.7 (8).

mL) and the solution layered with diethyl ether. The purple crystals that resulted (0.03 g) were washed with hexanes and diethyl ether and dried.[8] A solution of this product in 0.1 M *n*-Bu_4NPF_6–CH_2Cl_2 showed well-defined redox properties (as measured by the cyclic voltammetric technique) with $E_{1/2}(\text{ox}) = +1.17$ V, $E_{p,c} = -1.30$ V, and $E_{p,c} = -1.60$ V vs Ag/AgCl. For the oxidation at $E_{1/2} = +1.17$ V, $E_{p,a} - E_{p,c} = 150$ mV and $i_{p,a}/i_{p,c} = 1.0$ for $v = 200$ mV s^{-1}; under these same conditions there were no coupled oxidation waves associated with the reductions at −1.30 and −1.60 V. A single crystal of this compound was selected and subjected to an X-ray structure analysis. This complex proved to be the (organoimido)rhenium(V) complex Re(N-*n*-Pr)Br_3(dppbe), the structure of which is shown in Figure 1.[9–12]

The Re–N and N–C bond distances (1.719 (8) and 1.41 (1) Å, respectively) and the linearity of the Re–N–C angle (178.7 (8)°) are clearly in accord with an alkylimido moiety and an interaction best represented as[1a,13,14]

$$Re\equiv N-CH_2CH_2CH_3$$

This gives an 18-electron count for the metal center, and the absence of a structural trans effect for the Re–Br bond trans to Re(N-*n*-Pr) is therefore to be expected.[1a] To our knowledge, this is the first crystal structure determination on an (alkylimido)rhenium(V) complex where R is other than methyl.

The mechanism by which Re(N-*n*-Pr)Br_3(dppbe) is formed remains to be established. However, in view of the relative facility with which *trans*-$ReX_2(dppbe)_2$ is formed in the reactions between $(n\text{-}Bu_4N)_2Re_2X_8$ and dppbe in nitrile solvents, it is not unreasonable that a rhenium(I) intermediate is involved in the formation of Re(N-*n*-Pr)Br_3(dppbe). A four-electron oxidation of such an entity would then provide the four electrons necessary for the reduction of the nitrile ligand. Interestingly, there is a very recent report by Wilkinson and co-workers[15] in which the complex cation *trans*-$[CrCl(NCMe)(dmpe)_2]^+$ (dmpe = $Me_2PCH_2CH_2PMe_2$) is converted into *trans*-$[Cr(NEt)Cl(dmpe)_2]^+$ by a methanolic solution of $Ba(SO_3CF_3)_2$. The resulting chromium(IV) species, which is "isoelectronic" with Re(N-*n*-Pr)Br_3(dppbe), is apparently formed by a mechanism that is quite different from that by which the rhenium(V) complex is formed in *neat* propionitrile.

In view of the interest in the reduction of nitriles to give amines[16] and its reverse (i.e. the oxidation of coordinated amines to give nitriles),[17] our findings are of importance since imine intermediates are likely in both of these reactions. As a means of synthesizing alkylimido complexes this reaction is quite novel,[1a] and we are now examining the mechanistic and synthetic implications and the scope of this and related reactions. Full structural details will be published in due course.

Acknowledgment. Support from the National Science Foundation through Grant No. CHE85-06702 to R.A.W. and Grant No. CHE86-15556 for the purchase of the MICROVAX computer and diffractometer is gratefully acknowledged.

Supplementary Material Available: A table of atomic coordinates and an ORTEP view of Re(N-*n*-Pr)Br_3(dppbe) showing the full atomic numbering scheme (3 pages). Ordering information is given on any current masthead page.

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[8] The ^1H NMR spectrum of this complex (in $CDCl_3$) shows resonances at δ +1.42 (m, $NCH_2CH_2CH_3$), +0.70 (t, $NCH_2CH_2CH_3$), and −0.56 (m, $NCH_2CH_2CH_3$) that we attribute to the resonances of the alkylimido group. Like those in other (alkylimido)rhenium(V) complexes, the α-CH_2 group is subject to deprotonation to give $ReN{=}CHCH_2CH_3$. See: Chatt, J.; Dosser, R. J.; King, F.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1976**, 2435.

[9] Crystals of Re(NC_3H_7)Br_3(dppbe) are monoclinic, space group $P2_1/c$, with $a = 16.677$ (2) Å, $b = 10.852$ (2) Å, $c = 18.382$ (4) Å, $\beta = 95.81$ (1)°, $V = 3310$ (2) $Å^3$, $Z = 4$, $d_{calcd} = 1.833$ g/cm^3, and $\mu = 74.26$ cm^{-1}. X-ray diffraction data were collected at 22 °C on a 0.39 × 0.35 × 0.06 mm crystal for 4594 independent reflections having $4 < 2\theta < 45°$ on an Enraf-Nonius CAD4 diffractometer using graphite-crystal-monochromated Mo*Kα* radiation (λ = 0.71073 Å). Details of the crystal data collection and reduction methods are the same as those described elsewhere.[10] An empirical absorption correction was applied,[11] but no correction for extinction was made. During the course of the structure analysis, it became apparent that the CH_2CH_3 fragment of the *n*-propylimido ligand was disordered. This ligand is contained within a pocket that is formed by two of the phenyl rings of dppbe. A model was developed in which this fragment was disordered about the plane that contains the Br(2)–Re–N(1)–C(2) unit and bisects the bond C(11)–C(12) of the dppbe ligand (Figure 1). Half of the disorder is shown in Figure 1 with the alkyl chain C(2)–C(3)–C(4) (not shown) representing the other half. Consequently, atoms C(3), C(4), C(5), and C(6) reflect sites of half-occupancy. The rather large thermal parameters associated with C(3), C(4), C(5), and C(6) reveal some inadequacies in this model. Nonetheless, this is a satisfactory solution overall. All atoms except these four carbon atoms were refined anisotropically, and corrections for anomalous scattering were applied to these atoms.[12] Positions for the hydrogen atoms of the dppbe ligand were calculated by assuming idealized geometry and a C–H distance of 0.95 Å. While the hydrogen atoms were used in the calculation of F_o, they were not included in the least-squares refinement. The final residuals were $R = 0.055$ and $R_w = 0.079$ for 3135 data with $I > 3\sigma(I)$.

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Metalation and Transmetalation of a Binuclear Complex of Nickel(0). Molecular Alloys of Nickel and Palladium

Sir:

Metal–metal bonds between two or more different metal atoms are of fundamental interest.[1,2] The chemical and physical con-

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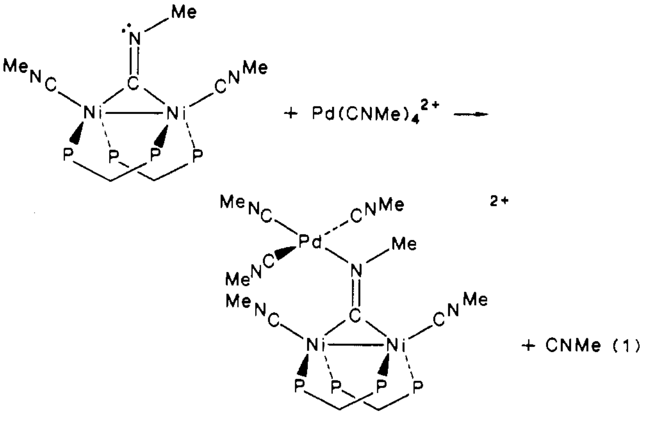
sequences of alloying different metals on a molecular level may include (i) cooperative reactivity, (ii) highly charge separated excited states, and (iii) unusual magnetic properties. Shaw and co-workers have been particularly active in the preparation of dppm-bridged (dppm = $PPh_2CH_2PPh_2$) heterobimetallic complexes via a synthetic strategy based on the transmetalation of relatively labile d^{10} metal ions, Cu^I, Ag^I, Au^I, or Hg^{II}, by d^8 ions such as Rh^I or Ir^I.[3] We describe here the metalation and transmetalation of the binuclear Ni(0) complex $Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2$ by Pd^{II}. The metalation substrate in these studies, $Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2$, possesses a μ-isocyanide ligand with N atom Lewis basicity exceeding that of ammonia.[4] We have therefore undertaken a study of the potential N atom metalation chemistry of the bridging isocyanide ligand of $Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2$. Our rather surprising findings and the synthesis of the first bi- and trinuclear complexes containing Ni–Pd bonds are described below.

Treatment of a benzene solution of $Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2$ with 1 equiv of $[Pd(CNMe)_4][PF_6]_2$[5] in acetonitrile leads to the metalated product $[Ni_2Pd(CNMe)_6(dppm)_2][PF_6]_2$ (**1**) in 94% yield.[6] Complex **1** exhibits only terminal isocyanide ν(CN) bands at 2170 and 2126 cm^{-1} (KBr). The $^{31}P\{^1H\}$ NMR spectrum of **1** in acetonitrile is an AA′BB′ spin system[3c,d] with two approximate quartet features centered at δ 28.7 and 0.8, $^2J_{AB} + {}^4J_{AB'} = 163$ Hz. In view of the N atom basicity of $Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2$, we anticipated an N-metalated product analogous to the aminocarbyne species reported previously (eq 1).[4] Microanalytical data are fully consistent and $^{31}P\{^1H\}$ and IR data are not inconsistent with the putative structure I. However the ^1H NMR spectrum of **1** indicates the presence of only two methyl isocyanide environments, in a ratio of 2:1, irrespective of temperature. The methyl isocyanide signals at δ 3.03 and 2.94 also appear as doublets with splittings of 3.9 and 2.8 Hz respectively. The apparent splittings are independent of magnetic field strength, vanish in the $^1H\{^{31}P\}$ spectrum, and are therefore assigned to long range $^5J(\overline{\mathrm{P{-}M{-}C{\equiv}N{-}CH_3}})$ coupling. Such long-range coupling has also been observed in the ^1H NMR spectra of $[Fe(CO)_2(PMe_3)_2(\eta^2\text{-}CMe{=}N{-}CMe_3)][BPh_4]$, $^5J(\overline{\mathrm{P{-}Fe{-}N{-}C{-}CH_3}}) = 2.4$ Hz[7] and $[(MeC{\equiv}C)Pt(\mu\text{-}dppm)_2(\mu\text{-}C{\equiv}CMe)Ir(CO)][PF_6]$, $^5J(\overline{\mathrm{P{-}Pt{-}C{\equiv}C{-}CH_3}}) = 2.0$ Hz.[8] Significantly, the ^1H NMR methyl isocyanide signals of **1** appear as long-range ^{31}P-coupled doublets, indicating only one dppm phosphorus atom shares the coordination sphere with both types of methyl isocyanide ligands. The ^1H NMR data clearly indicate that complex **1** is not fluxional and does not conform to structure I.



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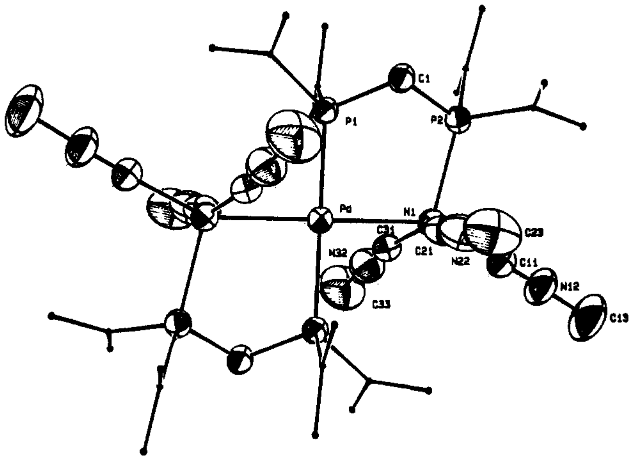

Figure 1. ORTEP diagram for **1** with 50% probability thermal ellipsoids. The first three carbons of each of the eight dppm phenyl rings are included in the drawing to indicate phenyl ring contours. Selected bond lengths (Å) and angles (deg) are as follows: Pd–Ni = 2.6087 (7), Pd–P1 = 2.337 (1), Ni–P2 = 2.287 (2), Ni–C11 = 1.884 (6), Ni–C21 = 1.846 (7), Ni–C31 = 1.846 (7), C11–N12 1.136 (7), C21–N22 = 1.160 (8), C31–N32 = 1.143 (8); Ni′–Pd–Ni = 180 (0), P1–Pd–Ni = 86.57 (4), P1–Pd–P1′ = 180 (0), P2–Ni–Pd = 101.47 (4), C11–Ni–Pd = 153.9 (2), C21–Ni–Pd = 75.4 (2), C31–Ni–Pd = 78.6 (2), C11–Ni–P2 = 104.1 (2), C21–Ni–P2 = 90.9 (2), C31–Ni–P2 = 117.6 (2), C11–Ni–C21 = 99.2 (3), C11–Ni–C31 = 93.7 (3), C21–Ni–C31 = 144.7 (3).

Crystals of **1** suitable for X-ray diffraction were obtained from a saturated toluene/acetonitrile mixed-solvent system.[9] The structure of the $Pd(CNMe)_4^{2+}$ metalation product, **1**, consists of a linear heterotrinuclear Ni–Pd–Ni unit with two dppm ligands oriented trans at the central palladium atom and spanning, in different directions, two outer Ni atoms. An ORTEP drawing of the $[Ni_2Pd(CNMe)_6(dppm)_2]^{2+}$ molecular cation is presented,

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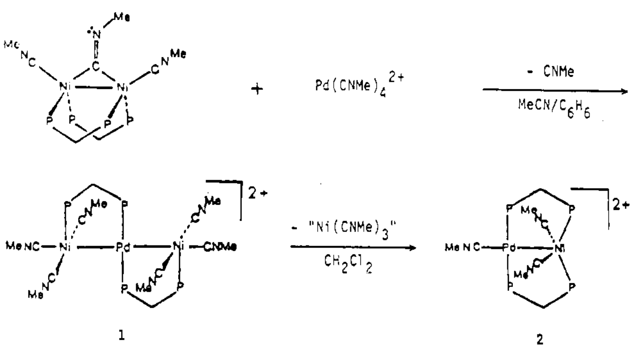
(9) Suitable crystals of **1** as the acetonitrile solvate, were obtained by cooling a saturated $MeCN/C_7H_8$ mixed solvent system. Crystallographic data for **1**·2MeCN: formula, $Ni_2PdC_{66}H_{68}F_{12}N_8P_6$; monoclinic, space group $P2_1/c$, $a = 11.954$ (3) Å, $b = 21.788$ (3) Å, $c = 14.060$ (2) Å, $\beta = 99.54$ (2)°, $V = 3611$ (2) Å^3, $d_{calcd} = 1.481$ g·cm^{-3} for $Z = 2$; Mo Kα $\gamma = 0.71073$ Å. Crystal dimensions were 0.72 × 0.25 × 0.22 mm^3. Intensity data were collected at 22 °C by the θ–2θ scan method in the range $4° \leq 2\theta \leq 45°$ on Enraf-Nonius CAD4 diffractometer. A total of 4839 unique data were collected over the following *h*, *k*, and *l*, limits: −12 to 12, 0 to 23, and 0 to 15. The structure was solved by MULTAN–least-squares–Fourier methods and was refined by full-matrix least-squares methods to yield final *R* and R_w values of 0.042 and 0.055 for 430 variables and 3245 observations with $I > 3.0\sigma(I)$. All programs were from the Enraf-Nonius SDP package. A complete description of the data collection parameters, structure solution and refinement conditions, atomic coordinates, bond distances and angles, thermal parameters, and structure factors are provided as supplementary material.

along with selected bond distances and angles, in Figure 1. The central Pd atom lies on an inversion center, and the Ni–Pd–Ni chain is therefore strictly linear. The Pd–Ni distances are 2.6087 (7) Å, slightly longer than the Pd–Pd distances of 2.5921 (5) Å found in the related homotrinuclear Pd complex $[Pd_3(CNMe)_6(PPh_3)_2][PF_6]_2$.[10] The Pd–Ni distance falls near the middle of the range generally reported for Pd–Pd σ bonds,[11,12] in spite of the smaller sum of van der Waals radii for a Pd–Ni interaction. Several other M–M′–M-bonded heterotrinuclear complexes have been reported in the past several years.[13] Homotrinuclear M–M–M-bonded complexes of Ni,[14a] Rh,[14b] and Pt[14c] have also been reported. Complex **1** contains the first structurally characterized Ni–Pd–Ni interaction that can be viewed as strongly bonding.

The palladium atom of **1** is in an approximately square-planar environment, surrounded by pairs of rigorously trans, symmetry-related phosphorus and nickel atoms. The nickel atoms are in distorted square-pyramidal environments in which three methyl isocyanides and the palladium atom comprise approximate equatorial planes, mutually cis to dppm phosphorus atoms. There is a pronounced bending of two of the methyl isocyanide carbon atoms, C21 and C31, toward the central palladium atom: ∠C21–Ni–Pd = 75.4 (2)°; ∠C31–Ni–Pd = 78.6 (2)°. A similar tendency toward semibridging methyl isocyanides was observed in $[Pd_3(CNMe)_6(PPh_3)_2][PF_6]_2$.[10] The structure of **1** is also related to a series of triphosphine,[15a–d] 2,6-diphosphinopyridine,[15e] and diphosphinoarsine[15f,g] metalla-macrocyclic homo- and heterotrinuclear complexes reported by Balch and co-workers.

In methylene chloride solution, the metalation product **1** undergoes a net elimination of $Ni(CNMe)_3$ to afford the transmetalated, heterobimetallic complex $[NiPd(CNMe)_3(dppm)_2][PF_6]_2$ (**2**). Complex **2** is obtained in 80% yield from **1**.[16] The IR spectrum of **2** reveals only terminal isocyanides, ν(CN) = 2220, 2184, and 2137 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum of **2** is an AA′BB′ system with predominant features centered at δ 8.0 and 2.6 with $^2J_{AB} + {}^4J_{AB'} = 124$ Hz, indicating inequivalent dppm phosphorus environments, similar to **1**. In the ^1H NMR spectrum, two types of methyl isocyanides are observed at δ 2.71 and 2.57, in a ratio of 2:1. An X-ray structural study of **2** was undertaken.[17]

Scheme I



The structure of **2** as the THF solvate could not be refined satisfactorily. The structure, however, is isomorphous with the recently reported structure of the "mixed-geometry" homobimetallic complex $[Ni_2(CNMe)_3(dppm)_2][PF_6]_2\cdot 3THF$.[4b] There is also a close similarity in spectroscopic data between the homo (M = M′ = Ni) and hetero (M = Pd, M′ = Ni) bimetallic $[MM'(CNMe)_3(dppm)_2][PF_6]_2$ complexes, with the notable exception of $^{31}P\{^1H\}$ NMR data, which are particularly sensitive to the presence of dissimilar metals.[4b,16]

The formation of **2** from $Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2$ and $[Pd(CNMe)_4][PF_6]_2$ represents a stepwise metalation and transmetalation of a binuclear nickel complex. The efficient conversion of **1** to **2** implies that **1** is an intermediate in the transmetalation process. The formation of **2** from **1** requires the formal elimination of $Ni(CNMe)_3$ from **1**. We have not been able to identify the fate of "$Ni(CNMe)_3$" eliminated in CH_2Cl_2 solution. However, we have observed that similar transmetalations in THF solution give $Ni(CNMe)_4$ as the primary coproduct[18a] and note that $Ni(CNMe)_4$ is unstable in CH_2Cl_2.[18b] The metalation and transmetalation chemistry of $Ni_2(\mu\text{-}CNMe)(CNMe)_2(dppm)_2$ is summarized in Scheme I.

The formation of **1** is sufficiently rapid that we have not been able to discern spectroscopically whether an N-metalated intermediate, structure I, is involved. The presence of alternative "open" structures, as in the equilibria of the closely related $Ni_2(CO)_x(dppm)_2$ ($x = 3$–5) complexes[19] raises the possibility of direct insertion of $Pd(CNMe)_4^{2+}$ into a Ni–Ni bond, followed by realignment of the dppm ligands. Direct metalation of an existing metal–metal bond has been observed in the formation of metal-bridged A-frame complexes.[20,21]

Our results provide an unusual illustration of the transmetalation of a binuclear complex via a trinuclear intermediate. The preparation of the first Ni–Pd-bonded heterometallic systems also provides a model for the preparation of longer chain metal–metal′-bonded molecular alloys.

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(16) $[NiPd(CNMe)_3(dppm)_2][PF_6]_2$ (**2**): A solution of **1** in CH_2Cl_2 was stirred under N_2 for ~24 h until the IR ν(CN) bands characteristic of **1** were replaced by new bands at 2226 (sh), 2202 (s), and 2152 (s) cm^{-1}. The resulting red solution was filtered to remove an insoluble yellow material, and the filtrate was concentrated under reduced pressure. Ether was added to facilitate precipitation, and the solution was cooled at −10 °C to obtain **2** as a red-purple solid in 80% yield. **2**: ^1H NMR (200 MHz, CD_2Cl_2) δ 7.3 (m, 40 H, Ph), 4.40 (s, 4 H, CH_2), 2.71 (s, 6 H, CNMe), 2.57 (s, 3 H, CNMe); $^{31}P\{^1H\}$ NMR (CH_2Cl_2, referenced to external 85% H_3PO_4) δ 8.0, 2.6 (AA′BB′, $^2J_{AB} + {}^4J_{AB'} = 124$ Hz); IR (KBr) ν(CN) 2220 (sh), 2184 (s), 2137 cm^{-1}(s). Anal. Calcd for $NiPdC_{56}H_{53}F_{12}N_3P_6$: C, 49.73; H, 3.94; N, 3.12. Found C, 49.62; H, 4.21; N, 2.99.

(17) Crystals of **2** as the tetrahydrofuran solvate were obtained by slow evaporation of a THF solution. Crystallographic data for **2**·3THF: formula, $NiPdP_6F_{12}O_3N_3C_{68}H_{77}$; monoclinic, space group $P2_1$, a = 13.733 (3) Å, b = 15.057 (4) Å, c = 18.122 (4) Å, β = 101.53 (1)°, V = 3671 (2) Å^3, d_{calcd} = 1.414 g·cm^{-3} for Z = 2; Mo Kα radiation, λ = 0.71073 Å. Intensity data were collected at 22 °C by the θ–2θ scan method in the range 4° ≤ 2θ ≤ 45° on an Enraf-Nonius CAD4 diffractometer. The unit cell and structure appear to be isomorphous with the recently reported dinickel analogue $[Ni_2(CNMe)_3(dppm)_2][PF_6]_2\cdot 3THF$.[4b] However the structure of **2**·3THF could not be refined satisfactorily owing to inability to contain the THF molecules of crystallization and eventual loss of crystallinity. Unsatisfactory refinement caused by a disordered $P2_1/m$ unit cell cannot be ruled out. Attempts at including mother liquor in the crystal capillary and low-temperature data collection were unsuccessful.

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Supplementary Material Available: Tables of crystal data and conditions for data collection, positional parameters, general temperature factors, bond distances, bond angles, and torsion angles (13 pages); listings of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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Characteristic Features of CO_2 Insertion into a Cu–H Bond. An ab Initio MO Study

Sir:

One of the current interests in the chemistry of transition-metal CO_2 complexes is the activation of carbon dioxide via direct coordination to metal complexes and the subsequent conversion to organic substances.[1] In this regard, there is a need to elucidate the electronic structure, bonding nature, and reactivity of transition-metal CO_2 complexes, in the hope of finding ones that are useful for CO_2 fixation. Several MO studies of transition-metal CO_2 complexes have been carried out;[2,3] however, to our knowledge, an MO study of the CO_2 conversion to organic substances has not been reported.

Chart I

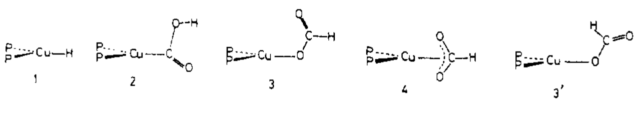

Table I. Relative Stabilities (kcal/mol) of Possible Products in CO_2 Insertion into the Cu–H Bond of $CuH(PH_3)_2$[a]

	basis set, method			
	small, HF	medium, HF	medium, MP2	large, HF
2	−15.5	−22.8	−19.8	−26.1
3	−37.4	−40.2	−29.0	−55.6
4	−36.8	−37.5	−29.1	−56.8

[a] The sum of the total energies of **1** and CO_2 is taken as a standard (zero energy).

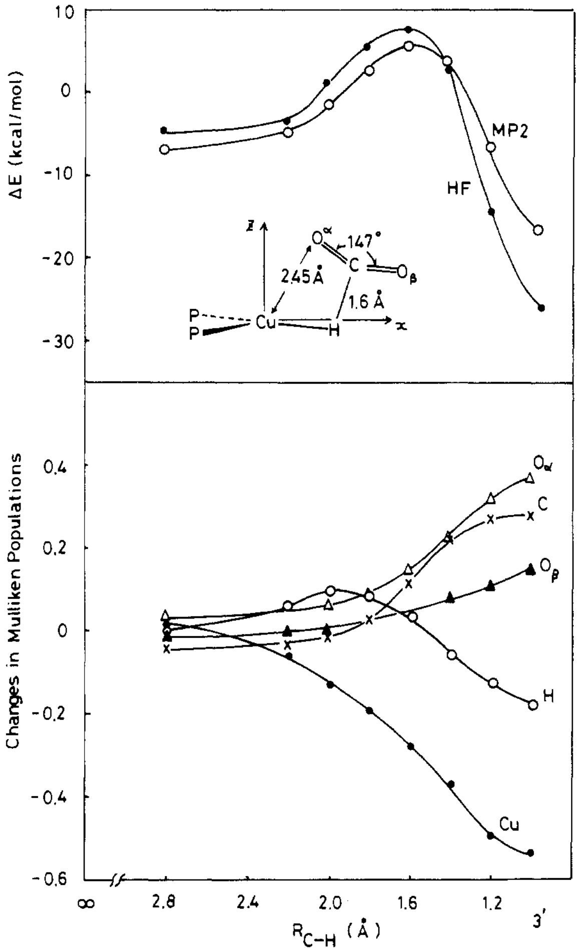

Figure 1. Changes in total energy and Mulliken populations caused by CO_2 insertion into the Cu–H bond (HF calculations with the medium basis set. The infinite separation of CO_2 and $CuH(PH_3)_2$ is taken as a standard (the value of zero on the ordinate scale).

In the present work, CO_2 insertion into a metal–hydride bond is investigated with an ab initio MO method. $CuH(PH_3)_2$ (**1**, Chart I) is chosen as a model,[4] because the CO_2 insertion into the Cu(I)–alkyl bond is well-known.[1e–i] Three complexes, $Cu(PH_3)_2(COOH)$ (**2**), $Cu(PH_3)_2(OCOH)$ (**3**), and $Cu(PH_3)_2(O_2CH)$ (**4**), are examined as possible products. This is the first example of a detailed MO study of the CO_2 insertion reaction, and several characteristic features of the reaction are clarified.

MO calculations were carried out with Gaussian 82[5] and IMSPACK[6] programs, where three kinds of basis sets were employed:

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