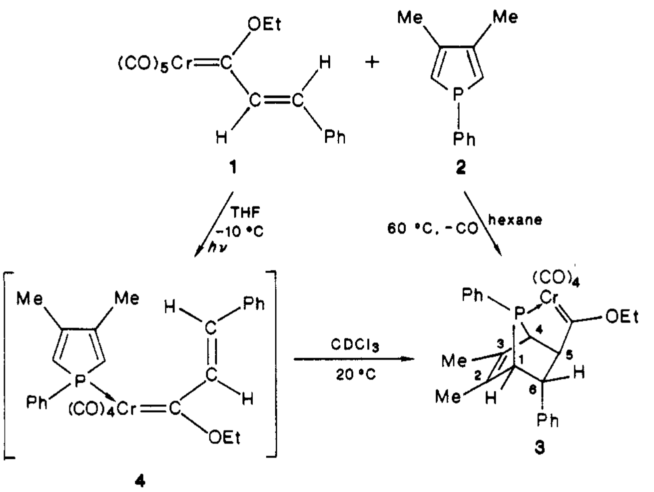
Scheme I



428 ($M^+ - 3CO$), 400 ($M^+ - 4CO$, 100). Its IR spectrum indicated a tetracarbonylchromium structure. Its ^1H and ^{13}C NMR spectra[6] confirmed the proposed formulation. The stereochemistry at C_6 was established on the basis of the ^1H NMR spectrum. Decoupling experiments showed a weak $^3J(H\text{–}C_1\text{–}C_6\text{–}H)$ coupling (ca. 1–2 Hz) which implies that H–(C_6) occupies the exo position. Thus, as expected, the Diels–Alder reaction takes place with retention of the stereochemistry at the C=C double bond of the dienophile. The first step of this reaction is the displacement by the λ^3-phosphorus of one cis CO on the chromium atom leading to the *cis*(vinyl ethoxycarbene)(1-phenyl-3,4-dimethylphosphole)tetracarbonylchromium complex 4 (Scheme I). Indeed, it proved possible to detect this intermediate compound 4 after its photochemical generation at −10 °C, in THF by irradiation with a TQ 150 Hanau medium-pressure lamp with a Pyrex filter. Under such conditions, the phosphole behaved as a classical phosphorus ligand toward a carbene complex.[7] This was also suggested by the following experiment. When we heated the [(phenylethoxy)carbene]pentacarbonyltungsten with a slight excess of phosphole 2 in hexane at 60 °C for 6 h we isolated the *cis*-(phosphole)(ethoxycarbene)tetracarbonyltungsten[8] in ca. 90% yield. Complex 4 is deep purple: its ^{31}P NMR spectrum displayed a single peak at 52 ppm (in THF). However, when we tried to record its ^1H NMR spectrum in $CDCl_3$, decomposition took place to give 3. This fact was confirmed by the ^{31}P NMR spectrum of the same sample which showed the presence of two peaks at 168 and 50.7 ppm ($CDCl_3$) and by the ^{13}C NMR spectrum which showed two carbenic carbon signals and the appearance of a phosphanorbornenyl system.[9]

It is interesting to note here that somewhat related intramolecular [4 + 2] cycloadditions between phosphole dienic systems and C=C double bonds within a single coordination sphere have already been described.[10]

We are currently exploring the possibilities offered by this approach as well as the reactivity of this new type of complex.

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(9) 4 → 3: ^{31}P NMR ($CDCl_3$) δ_P 168.0 (3) and 50.7 (4); ^{13}C NMR ($CDCl_3$) δ_C 14.9, 15.3, 15.9, 17.2, 17.4 (Me), 51, 56, 61, 66 (CH and OCH_2 of 3), 334.2 (C=Cr of 4), 356.3 (C=Cr of 3).

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Sequential Insertion of CO into Rhodium–Nitrogen μ-Imido/Amido Bonds: Formation of Isocyanate and Dimetallocycloimide Complexes[1]

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Summary: Treating $Rh_2(\mu\text{-NHMe})(CO)_2(\mu\text{-dppm-H})(\mu\text{-dppm})$ (dppm-H = bis(diphenylphosphino)methanide; dppm = bis(diphenylphosphino)methane) or tautomeric mixtures of $Rh_2(\mu\text{-NHR})(CO)_2(\mu\text{-dppm-H})(\mu\text{-dppm})$ and $Rh_2(\mu\text{-NR})(CO)_2(\mu\text{-dppm})_2$ (R = *p*-MePh or Ph) with 1 equiv of CO gives $Rh_2(\mu\text{-}\eta^2\text{-RNCO})(CO)_2(\mu\text{-dppm})_2$ (R = Me, *p*-MePh, or Ph). With excess CO $Rh_2(\mu\text{-CO})(CO)_2(dppm)_2$, RNCO, and $(RHN)_2CO$ are obtained for R = *p*-MePh or Ph. With R = Me, $Rh_2[\mu\text{-}\eta^2\text{-C(O)N(Me)C(O)}](\mu\text{-CO})(CO)_2(dppm)_2$ and $Rh_2(\mu\text{-CO})(CO)_2(dppm)_2$ are obtained.

Catalytic carbonylations of organoazides and nitroaryls are frequently postulated to proceed via metal imido intermediates.[2] In support of this proposal imido complexes have been isolated from reactions of metal complexes with organoazides, nitroaryls, and nitrosoaryls.[3] In the catalytic processes the formation of nitrogen–carbon bonds is a key step. In most cases, isocyanate (formed by coupling of the imido ligand and CO) is the final product or is a probable precursor to the final product. However, until recently[3a] the isolated imido complexes have given little, if any, isocyanates or products derived from isocyanates when treated with CO under mild conditions.[4] This communication reports the facile formation of isocyanate and dimetallocycloimide complexes and free isocyanates and ureas by the formal single and double insertion of CO into the metal–nitrogen bonds of rhodium μ-imido/amido A-frame complexes.

Previously we reported the preparation and characterization of $Rh_2(\mu\text{-NHR})(CO)_2(\mu\text{-dppm-H})(\mu\text{-dppm})$ (1, R = Me, dppm-H = bis(diphenylphosphino)methanide, dppm = bis(diphenylphosphino)methane) and tautomeric mixtures of 1 and $Rh_2(\mu\text{-NR})(CO)_2(\mu\text{-dppm})_2$ (2, R = *p*-MePh or Ph).[5] When solutions (CH_2Cl_2, toluene or benzene) of

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(1) Part 3 in a series entitled *Late Transition Metal μ-Oxo and μ-Imido Complexes*. For part 2 see ref 5.

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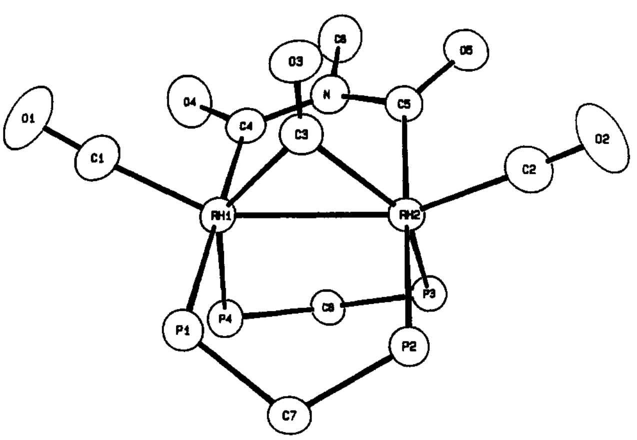
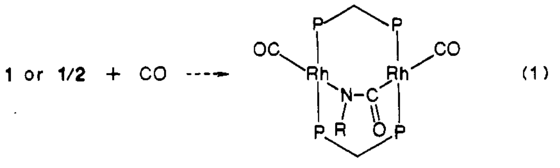


Figure 1. ORTEP view of $Rh_2[\mu\text{-}\eta^2\text{-}C(O)N(Me)C(O)](\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2$ (4), 50% probability ellipsoids. Phenyl rings omitted. Selected distances (Å) and angles (deg): Rh1–Rh2, 2.714 (1); Rh1–C4, 2.076 (6); Rh2–C5, 2.047 (6); C4–O4, 1.216 (6), C5–O5, 1.215 (6); C4–N, 1.390 (7); C5–N, 1.407 (7); N–C6, 1.472 (7); Rh2–Rh1–C4, 85.3 (2); Rh1–Rh2–C5, 86.7 (2); Rh1–C4–O4, 121.2 (4); Rh2–C5–O5, 124.5 (4); Rh1–C4–N, 120.9 (4); Rh2–C5–N, 118.4 (4); N–C4–O4, 118.0 (5); N–C5–O5, 117.1 (5); C4–N–C5, 123.6 (5); C4–N–C6, 117.6 (5); C5–N–C6, 118.1 (5).

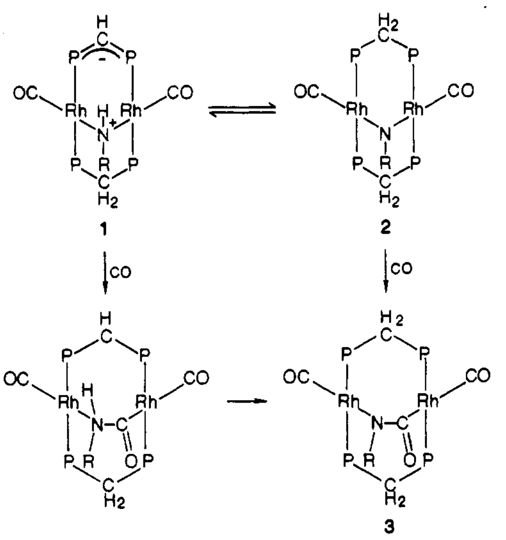
1 or 1/2 are treated with 1 equiv of CO (1 atm, 22 °C), a rapid reaction (seconds for R = Me or *p*-MePh and minutes for R = Ph) occurs giving a single new product formulated as $Rh_2(\mu\text{-}\eta^2\text{-RNCO})(CO)_2(\mu\text{-dppm})_2$ (**3**, R = Me, *p*-MePh, or Ph, eq 1).[6,8,9] With R = *p*-MePh or Ph, **3** is unstable and decomposes on standing (hours, free isocyanate is observed) or on attempted isolation. With R = Me, **3** is more stable and solid samples have been isolated (80%). With ^{13}CO, the ^{13}C label is scrambled over all three carbonyl sites (the two terminal CO ligands and the RNCO) of **3** and any remaining **1**/**2** is ^{13}CO enriched. This suggests rapid CO exchange prior to insertion. The ^{13}C NMR spectrum of ^{15}N- and ^{13}C-labeled **3** (R = Ph) shows ^{13}C–^{15}N coupling consistent with the structure proposed in eq 1.[6]



3

P⌒P = dppm; R = Me, *p*-MePh, or Ph

Scheme I



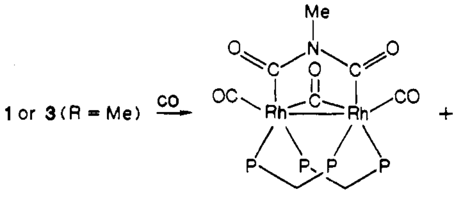
Excess carbon monoxide reacts with **1**/**2** or **3** (R = *p*-MePh or Ph) to give $Rh_2(\mu\text{-CO})(CO)_2(dppm)_2$[10] as the only major metal-containing product (eq 2, 75% isolated yield).

$$1/2 \text{ or } 3 \xrightarrow{CO} Rh_2(\mu\text{-CO})(CO)_2(dppm)_2 + RNCO + (RHN)_2CO \quad (2)$$

$$R = p\text{-MePh or Ph}$$

The major organic products RNCO and $(RNH)_2CO$[11] are obtained in yields of 25 and 50% for R = *p*-MePh and 6 and 75% for R = Ph. The source of the hydrogens for the $(RHN)_2CO$ formation is unknown at this time.

Excess CO also reacts with **1** or **3** (R = Me), but two metal-containing products are obtained: $Rh_2(\mu\text{-CO})(CO)_2(dppm)_2$ (~33%) and yellow **4** (~60%, eq 3).



4

$Rh_2(\mu\text{-CO})(CO)_2(dppm)_2$ (3)

Spectroscopic[12] and X-ray data[13] show **4** to be the dimetallocycloimide, "cradle"[14] complex $Rh_2[\mu\text{-}\eta^2\text{-}C(O)N\text{-}$

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[6] All data were taken at 30 ± 5 °C. **3** (R = Me): IR (cm^{-1}, CH_2Cl_2) 1963 vs, 1946 s (ν_{CO}); IR (cm^{-1}, mineral oil) 1954 sh, 1938 s (ν_{CO}), 1094 m, 996 w (ν_{PC}), (no RNCO bands could be identified); ^{1}H NMR (90 MHz, C_6D_6/CD_2Cl_2) δ 7.86–6.78 (m, 40, Ph), 3.41, 3.17 (m, 2 each, CH_2), 1.78 (s, 3, CH_3); ^{13}C NMR (66 MHz, C_6D_6/CD_2Cl_2, ^{13}CO enriched) δ 203 (m, MeNCO),[7] 200 (d of t, J_{RhC} = 57 Hz, J_{PC} = 13 Hz, CO), 196 (d of t, J_{RhC} = 64 Hz, J_{PC} = 14 Hz, CO′); ^{31}P (121 MHz, toluene, external H_3PO_4 reference) δ 24.6 (d of m, J_{RhP} ~ 143 Hz), 22.6 (d of m, J_{RhP} ~ 174 Hz). Data for R = *p*-MePh and Ph is included as supplementary material.

[7] This chemical shift value is typical of carbamoyl ligands and is reasonable for **3** viewed as a metal substituted carbamoyl. See: Angelici, R. J.; Formanek, T. *Inorg. Chim. Acta* **1983**, *76*, L9–L11.

[8] The *trans,trans*-diphosphine A-frame geometry is assigned on the basis of the presence of one major ν_{PC} band in the IR of **3**. See footnote 11 in: Wu, J.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1987**, *16*, 1805–1807.

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[11] Organic products were detected and quantified by FTIR of the reaction mixtures and HPLC and GCMS of methanol quenched reaction mixtures.

[12] **4**: IR (cm^{-1}, mineral oil) 1999 s, 1984 vs (terminal ν_{CO}), 1787 s (bridging ν_{CO}), 1620, 1567 (imide ν_{CO}, assignment based on shifts with ^{13}C substitution), 1093 m, 994 m (cis ν_{PC}); ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.67–6.67 (m, 40, Ph), 3.98, 3.54, 3.16, 2.59 (m, 1 each, CH_2), 2.09 (s, 3, CH_3); ^{13}C NMR (66 MHz, CD_2Cl_2, ^{13}CO enriched) δ 241 (quint of t, J_{RhC} = J_{PC} = 42 Hz, J_{PC} = 11 Hz, μ-CO), 191 (m, imide CO), 190 (d of t, J_{RhC} = 77 Hz, J_{PC} = 10 Hz, terminal CO); ^{31}P (121 MHz, CD_2Cl_2, external H_3PO_4 reference) δ 31.8, 15.1 (m, P).

[13] Crystals from CH_2Cl_2: $Rh_2P_4O_5NC_{56}H_{47}\cdot CH_2Cl_2$, fw = 1,228.64, triclinic ($P\bar{1}$) with a = 12.117 (3) Å, b = 20.344 (4) Å, c = 11.160 (3) Å, α = 98.53 (2)°, β = 102.21 (2)°, γ = 91.21 (2)°, V = 2655.3 Å^3, Z = 2, and d_{calcd} = 1.54. Full-matrix least-squares calculations converged to $R(F_o)$ = 0.046 and $R_w(F_o)$ = 0.058 for 4612 independent observations (θ–2θ scan) above 3σ. Full structural details will be reported in a forthcoming publication.

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(Me)C(O)](μ-CO)(CO)$_2$(dppm)$_2$. A view of the molecular structure of **4** is given in Figure 1. To our knowledge **4** is the first example of a dimetallocycloimide. Its formation by sequential coupling of two CO molecules with an imido ligand is unique. A metallocycloimide, Cp$_2$W[C(O)N(Me)C(O)], was recently obtained from Cp$_2$WCO and MeNCO.[15]

The key step in the formation of the coordinated isocyanate is the carbon–nitrogen bond formation. A critical question in our system is which species, **1** or **2**, is actually involved in this step. A single step, insertion of CO into the Rh–imido bond, is all that is required for isocyanate formation from **2**. Two steps are required for **1**, insertion of CO into the Rh–amido bond to form a carbamoyl followed by proton transfer to the methanide. These two alternate pathways are illustrated in Scheme I. Though rare, insertion of CO into transition-metal amido bonds[16] and deprotonation of a carbamoyl (by an external base)[17] are known processes. We are attempting to answer this question by studying the reactions of [Rh$_2$(μ-NHR)(CO)$_2$(μ-dppm)$_2$]$^+$ with CO.

Acknowledgment. We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work and Johnson Matthey for a loan of RhCl$_3$. The National Science Foundation provided a portion of the funds for the purchase of the X-ray (CHE-7820347) and NMR (PCM-8115599) equipment. We thank Dr. H. Grasz for some of the NMR experiments and Professors E. Maatta and R. Angelici for helpful discussions.

Supplementary Material Available: Tables of crystal and data collection parameters, fractional coordinates, thermal parameters, spectroscopic data, hydrogen atom positions, and least-squares planes (10 pages); a listing of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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Two Novel Rhodium(I) Metallacycles from the New Heterodifunctional Ligand Me$_3$SiN=PPh$_2$CH$_2$PPh$_2$. An Example of the Formation of a Unique Iminato Nitrogen–Rhodium σ Bond

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Summary: The new heterodifunctional phosphine imine ligand, Me$_3$SiN=PPh$_2$CH$_2$PPh$_2$, reacts with [RhCl(cod)]$_2$ to form $\overline{\mathrm{NPPh_2CH_2PPh_2Rh}}$(cod) which contains a unique Rh$^{\mathrm{I}}$–N σ bond and with [RhCl(CO)$_2$]$_2$ to form Me$_3$Si$\overline{\mathrm{N{=}PPh_2CH_2PPh_2Rh}}$(CO)Cl. The new metallacycles have been characterized by means of complete ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR studies.

The new heterobifunctional ligand,[1] Me$_3$SiN=PPh$_2$CH$_2$PPh$_2$, may react in several different ways: (a) monodentate ligation at either trivalent N or P; (b) bidentate (chelate or bridging) coordination; (c) metal–nitrogen σ bond formation by means of the loss of a trimethylsilyl group;[1] or combinations of these possibilities. The varied behavior of this ligand offers considerable scope for the formation of useful homogeneous catalysts because the phosphane which has a predisposition for combination with soft metals (i.e., "late" transition metals or metals in low oxidation states) is juxtaposed with a "hard" nitrogen center (which is predisposed to combination with "early" transition metals or metals in high oxidation states). Chelation introduces the possibility that the more weakly bound center may be dissociated reversibly without total detachment of the ligand, thus opening reactive sites at the metal. The considerable catalytic activity of Rh$^{\mathrm{I}}$ species in particular[2-16] prompted an investigation of the chemistry of this metal with our new ligand. We find marked differences in reactivity with two rhodium(I) precursors leading in each case to novel Rh$^{\mathrm{I}}$ metallacycles.

When **1** reacts[17] with [Rh(cod)Cl]$_2$, Me$_3$SiCl is eliminated to form **2** which contains a Rh–N σ bond. The

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(17) (a) Complex **2** was formed when a solution of **1** (0.276 g, 5.88 mmol)[1] in dry dichloromethane (30 mL) was added dropwise (15 min) to a stirred dichloromethane (25 mL) solution of [Rh(cod)Cl]$_2$ (0.145 g, 2.94 mmol) at room temperature. An instantaneous color change from yellow-orange to pale yellow occurred on mixing, but the mixture was stirred at room temperature for 4 h before the solvent was removed in vacuo to yield an analytically pure dichloromethane solvate of **2** (yield 0.36 g; 90%; yellow crystals; mp 185 °C dec; yellow crystalline solid). Anal. Calcd for C$_{34}$H$_{34}$Cl$_2$NP$_2$Rh: C, 58.97; H, 4.91; N, 2.02; Cl, 10.24. Found: C, 58.85; H, 4.94; N, 2.02; Cl, 10.13. ^{31}P NMR (161.98 MHz in CDCl$_3$): $\sigma_{\mathrm{P^{III}}}$ 32.97 vs 85% H$_3$PO$_4$ (dd, $^{1}J_{\mathrm{PRh}}$ = 158.65, $^{2}J_{\mathrm{PP}}$ = 44.1 H$_2$), $\sigma_{\mathrm{P^{V}}}$ 52.17 (dd, $^{2}J_{\mathrm{PRh}}$ = 7.50, $^{2}J_{\mathrm{PP}}$ = 44.1 Hz). ^{1}H NMR (200 MHz, CDCl$_3$): phenyl rings δ 7.25, 7.55, 7.90 (m, 20 H); P*CH*$_2$P methylene δ 3.80 (dd, 2 H, $^{2}J_{\mathrm{HP}}$ = 11.08, 7.9 Hz); cod olefinic δ 5.35 (br, 2 H), 5.35 (br, 2 H); cod methylene δ 2.30 (br, 4 H), 1.75 (br, 4 H). (b) Complex **3** was prepared from [Rh(CO)$_2$Cl]$_2$ under similar experimental conditions to those described above. (yield 85%; orange crystals; mp 165 °C dec). Anal. (**3**·CH$_2$Cl$_2$) Calcd for C$_{30}$H$_{33}$NCl$_3$OP$_2$RhSi: C, 49.84; H, 4.56; N, 1.93; Cl, 14.72. Found: C, 50.02; H, 4.50; N, 1.95; Cl, 14.82. IR (Nujol): ν(CO) 1969. ^{31}P NMR (161.98 MHz in CDCl$_3$): $\sigma_{\mathrm{P^{III}}}$ 37.64 vs H$_3$PO$_4$ (dd, $^{1}J_{\mathrm{PRh}}$ = 168.6, $^{2}J_{\mathrm{PP}}$ = 31.1 Hz), $\sigma_{\mathrm{P^{V}}}$ 24.36 (dd, $^{2}J_{\mathrm{PRh}}$ = 4.0, $^{2}J_{\mathrm{PP}}$ = 31.1 Hz). ^{1}H NMR (400 MHz, CDCl$_3$): phenyl rings δ 7.30, 7.50, 7.75 (m, 20 H); P*CH*$_2$P methylene δ 3.71 (t, 2 H, $^{2}J_{\mathrm{HP}}$ = 9.7 Hz). ^{29}Si NMR (INEPT) (79.5 MHz, CDCl$_3$): δ 6.04 (d, 1 Si, $^{2}J_{\mathrm{PSi}}$ = 5.2 Hz).

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