(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.

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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, $^1J_{\mathrm{PRh}}$ = 158.65, $^2J_{\mathrm{PP}}$ = 44.1 H$_2$), $\sigma_{\mathrm{P^{V}}}$ 52.17 (dd, $^2J_{\mathrm{PRh}}$ = 7.50, $^2J_{\mathrm{PP}}$ = 44.1 Hz). ^{1}H NMR (200 MHz, CDCl$_3$): phenyl rings δ 7.25, 7.55, 7.90 (m, 20 H); PCH_2P methylene δ 3.80 (dd, 2 H, $^2J_{\mathrm{HP}}$ = 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, $^1J_{\mathrm{PRh}}$ = 168.6, $^2J_{\mathrm{PP}}$ = 31.1 Hz), $\sigma_{\mathrm{P^{V}}}$ 24.36 (dd, $^2J_{\mathrm{PRh}}$ = 4.0, $^2J_{\mathrm{PP}}$ = 31.1 Hz). ^{1}H NMR (400 MHz, CDCl$_3$): phenyl rings δ 7.30, 7.50, 7.75 (m, 20 H); PCH_2P methylene δ 3.71 (t, 2 H, $^2J_{\mathrm{HP}}$ = 9.7 Hz). ^{29}Si NMR (INEPT) (79.5 MHz, CDCl$_3$): δ 6.04 (d, 1 Si, $^2J_{\mathrm{PSi}}$ = 5.2 Hz).

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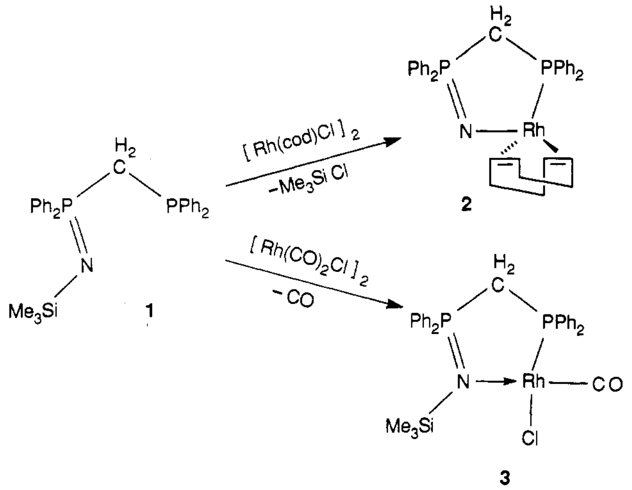

reaction is smooth, and the yield is almost quantitative. The iminato nitrogen center thus yields a unique example of a Rh(I)–N bond. Phosphine iminato ligands of the type $R_3P{=}NR$ in general coordinate as 1-, 2-, or 4-electron donors with low oxidation state "late" transition metals[18–21] and not in the way encountered here. Rh(I)–N σ bond formation (with any type of nitrogen) is also notable in that only a few examples of such bonding have been reported. The consequences of this structural feature in the ^{31}P NMR (Figure 1) spectral behavior are remarkable (vide infra).

In contrast, the carbonyl dimer $[Rh(CO)_2Cl]_2$ reacts differently losing 1 mol of CO to form the chelate **3** also in nearly quantitative yield.[17] Here the nitrogen atom acts as a normal 2-electron Lewis base to form a coordinate bond with Rh^I, a situation which, for Rh^I, is also relatively rare.

The difference in products formed in the two reactions can be attributed to the different nature of the CO and cod ligands. We presume that the first step of the reaction is the formation of a monomeric complex via monodentate coordination of the ligand through the phosphane end. Displacement of the relatively labile CO by the nitrogen base yields a stable 16-electron complex which cannot then eliminate Me_3SiCl to form an imide unless another ligand can be provided to stabilize the formally 14-electron imide product. In contrast cod is not as easily displaced completely so in this case a sequence can be visualized in which the nitrogen donor site coordinates to the Rh^I center forcing the cod substituent to act as a 2-electron donor. This intermediate may eliminate Me_3SiCl to form the imide **2** which is immediately stabilized as a 16-electron species by reestablishment of the cod as a 4-electron donor.

Both new complexes are air-stable crystalline solids for which satisfactory analytical data[17] have been obtained. They are relatively soluble in typical organic solvents and are monomeric in solution. Full NMR spectrometric analysis yields considerable insight into the bonding character of the compounds. Phosphorus-31 NMR (Figure 1) of both compounds show that the trivalent PPh_2 group is directly bound to Rh^I because of the large $^1J_{RhP}$ values (159 (**2**), 169 Hz (**3**)). The ^{31}P NMR chemical shifts for the directly bound PPh_2 phosphorus atoms in both compounds are also similar (approximately 35 ppm), giving a low-field coordination shift (vs the free ligand) of about 50 ppm.

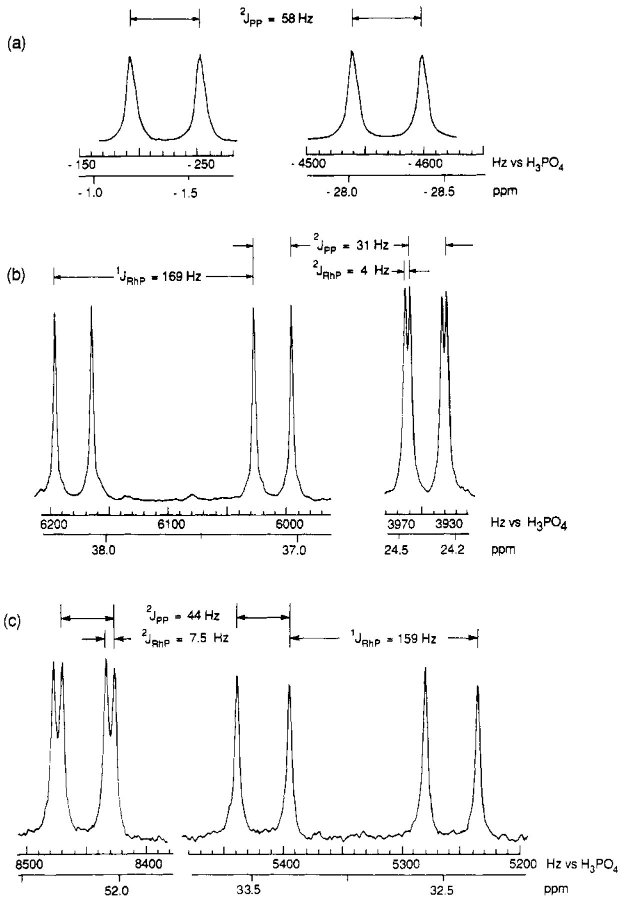

Figure 1. Fourier transform ^{31}P NMR (161.98 MHz) of the (a) parent phosphine imine $Me_3SiN{=}PPh_2CH_2PPh_2$, (b) complex **3**, and (c) the (iminato)rhodium complex **2** at normal probe temperatures in $CDCl_3$.

The remote phosphorus atom in the $-N{=}PPh_2-$ unit shows, in both cases, a small coupling with Rh ($^2J_{PRh}$ = 7.50 (**2**) and 4.0 Hz (**3**)). Both compounds show $^2J_{PP}$ (44.1 (**2**) and 31.2 Hz (**3**)) coupling in each part of the spectrum. The chemical shifts of the iminato phosphorus in the new compounds are however remarkably different. For **3** the chemical shift of +24 ppm, 25 ppm to low field of the parent compound **1**, is, as expected, a lower coordination shift compared to that shown by the phosphorus atom of the directly coordinated trivalent PPh_2 group. In contrast the signal for the iminato phosphorus in **2** is found at 52 ppm, thus giving an enormous shift of 53 ppm downfield from the free ligand **1** in spite of the fact that this phosphorus is not directly bound to the metal. We attribute this behavior to delocalization of electron density in the P=N—M framework.

Further spectral characterization of **3** was provided by the ^{13}C spectrum of the CO carbon which showed a $^1J_{RhC}$ of 68.5 Hz ($\sigma_{^{13}C}$ 188.7) and $^2J_{CP}$ of 17.5 Hz indicative of a cis relationship between the CO and P^{III} ligands. Further support for the cis structure of **3** is given by ν_{CO} = 1969 cm^{-1}. ^1H, ^{13}C, and ^{29}Si NMR are consistent with the structures illustrated.

The new compounds provide unique examples of the iminato nitrogen acting as both a 2-electron Lewis base and as a univalent anion bound to Rh^I to give 16-electron Rh species. Further studies are in progress to delineate

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the reactivity of these new systems, especially with regard to their homogeneous catalysis activity.

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Isolation of *cis*-Dimethyl(methoxycarbonyl)(triphenylphosphine)gold(III)

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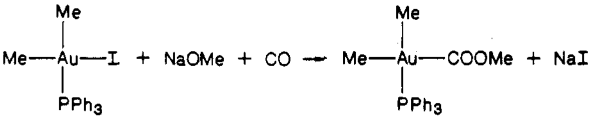
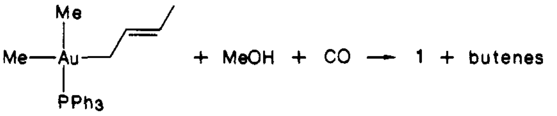
Summary: *cis*-Dimethyl(methoxycarbonyl)(triphenylphosphine)gold(III) (**1**) has been prepared by the reaction of carbon monoxide with a mixture of *cis*-dimethyliodo(triphenylphosphine)gold(III) and sodium methoxide in methanol. Thermolysis of **1** results in the competitive reductive elimination of methyl acetate and ethane.

In spite of extensive investigations on the structure and chemical reactivity of organogold(III) complexes,[1] only a few insertion reactions of unsaturated molecules such as sulfur dioxide have been reported.[2] Carbon monoxide is known to be unreactive toward any type of organogold(I) or -(III) complex, but a simple carbon monoxide coordinated gold(I) compound, AuCl(CO), has been described.[3] In the course of our studies on the preparation of organogold(III) complexes,[4] we found the formation of *cis*-dimethyl(methoxycarbonyl)(triphenylphosphine)gold(III) by the reaction of dimethyliodo(triphenylphosphine)gold(III) with carbon monoxide in the presence of sodium methoxide.

A methanol solution (22 mL) of *cis*-dimethyliodo(triphenylphosphine)gold(III) (96.6 mg, 0.157 mmol) in the presence of a slight excess of sodium methoxide (12.5 mg, 0.231 mmol) was treated with an excess of carbon monoxide at atmospheric pressure at 50 °C for 30 min to give a pale yellow, homogeneous solution. After evaporation of volatiles, colorless crystals of *cis*-dimethyl(methoxycarbonyl)(triphenylphosphine)gold(III) (1) were obtained by recrystallization of the residual solid.[5] This is the first example of the *formal* insertion of carbon monoxide for the organogold complexes. Complex 1 is air and thermally stable. Complex 1 also was obtained by the reaction of *cis*-dimethyl(η^1-(*E*)-crotyl)(triphenylphosphine)gold(III)[6] (**2**; 100.7 mg, 0.185 mmol) with an excess of carbon monoxide at atmospheric pressure in methanol (15 mL) at 50 °C for 30 min. (59%). A facile and selective methanolysis of the η^1-crotyl group at the γ-carbon in **2** with liberation of butenes,[6] gave a dimethylmethoxogold(III) intermediate which reacted further with carbon monoxide to give 1. Unfortunately, attempted isolation of the dimethylmethoxogold(III) intermediate was unsuccessful, and the only isolable material was trimethyl(triphenylphosphine)gold(III), probably due to the facile disproportionation of the intermediate compound.



$$\mathrm{Me{-}\overset{Me}{\underset{PPh_3}{Au}}{-}I} + \mathrm{NaOMe} + \mathrm{CO} \longrightarrow \underset{\mathbf{1}}{\mathrm{Me{-}\overset{Me}{\underset{PPh_3}{Au}}{-}COOMe}} + \mathrm{NaI} \qquad (1)$$



(2)

The ^{1}H NMR spectrum of 1 shows two doublets at 0.23 and 1.17 ppm, which are assignable to cis and trans gold methyl groups for a typical square-planar *cis*-dimethylgold(III) complex. A signal due to the methoxycarbonyl group appears at 3.17 ppm as a singlet, as in other transition-metal alkoxycarbonyl complexes.[7]

The $^{13}C\{^1H\}$ NMR spectrum of 1 also shows two doublets at 4.07 and 9.67 ppm for cis and trans gold methyl groups. The carbonyl carbon signal appears as a doublet at 210.7 ppm with a small coupling constant (^2J(P–C) = 11.9 Hz) with the phosphorus nucleus, suggesting that the methoxycarbonyl group occupies a coordination site cis to the triphenylphosphine ligand. The IR spectrum of 1 shows ν(C=O) at 1637 cm^{-1} as expected for a metallocarboxylate.[7]

At present, the mechanism of the formal insertion is not clear, whether carbon monoxide really inserts into the gold–methoxide bond or the reaction proceeds through the nucleophilic interaction of methoxide anion with coordinated carbon monoxide, since the dimethylmethoxogold(III) complex could not be isolated. However, the dimethylmethoxogold(III) complex is considered to be formed in methanol at least, since the reaction of an excess of methyl iodide with the complex prepared in situ afforded dimethyl ether (52%/Au) and *cis*-dimethyliodo(triphenylphosphine)gold(III) (52%/Au). In fact, 1 can be prepared by the reaction of carbon monoxide with a methanol solution of the dimethylmethoxogold(III) species prepared beforehand in situ. Thus, we prefer the insertion mechanism, although there is no direct experimental evidence for this. Note also that similar preferential insertion into the platinum–oxygen bond has been discussed in the case of some alkylalkoxoplatinum(II) complexes.[8]

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[5] Complex 1 was purified by recrystallization from ether/hexane: yield 59%; mp 124–125 °C dec. Anal. Calcd for $C_{22}H_{24}O_2PAu$: C, 48.19; H, 4.41. Found: C, 48.63; H, 4.60. ^{1}H NMR ($CDCl_3$): δ 0.23 (d, 3 H, ^3J(H–P) = 7.8 Hz, AuMe cis to P), 1.17 (d, ^3J(H–P) = 8.6 Hz, 3 H, AuMe trans to P), 3.71 (s, 3 H, OMe), 7.3–7.6 (m, 15 H, PPh_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 4.07 (d, ^2J(C–P) = 6.1 Hz, AuMe cis to P), 9.67 (d, ^2J(C–P) = 106.2 Hz, AuMe trans to P), 49.4 (s, OMe), 128–135 (m, PPh_3), 210.7 (d, ^2J(C–P) = 11.9 Hz, COOMe). IR (KBr): ν(C=O) 1637 cm^{-1}.

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