The isomeric mixture **5a** $\rightleftharpoons$ **5b** exhibits rather low thermal stability, and when the mixture is heated in acetone at temperatures around 40 °C, it provides, together with some insoluble, unidentified material, a third isomeric species, **6**, in which the isonitrile has formally migrated from the benzylic to the arylic position. Although complex **6** has been fully characterized,[13] little is presently known about the mechanism of this unusual and interesting transformation, which to our knowledge represents a rare example of a reversible isocyanide insertion into a transition-metal–carbon bond.[14]

Compounds **4** and **5** have a Ni–aryl bond and are therefore susceptible to undergo further insertion chemistry. Because of the simplicity of the CNXy system, **4** has been chosen for this study and has been carbonylated under ambient conditions. Interestingly, the reaction does not stop at the acyl stage and a vinyl complex of nickel, **7**, derived from a *N*-aryl-1-isoquinolone, is instead obtained (Scheme III).[15] The reaction clearly proceeds by insertion of CO into the Ni–aryl bond, followed by coupling of the acyl and imidoyl functionalities[16] in a process closely reminiscent of the well-known synthesis of cyclic amides catalyzed by organometallics reagents.[17] As shown in Scheme III, the organic ligand in the molecules of **7** can be freed by hydrolytic cleavage.

In conclusion the work described in this paper shows that binuclear complexes of nickel bridged by a hydrocarbon fragment containing a pseudoallyl and an aryl functionality display an interesting chemical behavior, in particular in reactions with isocyanides. Further studies on these and other related reactions are in progress.

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Registry No. **1a**, 137515-87-8; **1b**, 137540-20-6; **1c**, 137515-93-6; **2b**, 137515-88-9; **2c**, 137515-94-7; **3**, 137515-89-0; **4**, 137540-19-3; **5a**, 137515-90-3; **5b**, 137515-95-8; **6**, 137515-91-4; **7**, 137515-92-5; **8**, 137515-86-7; *o*-$BrCH_2C_6H_4Br$, 3433-80-5; *m*-$BrCH_2C_6H_4Br$, 823-78-9; *p*-$BrCH_2C_6H_4Br$, 589-15-1; CNXy, 2769-71-3; $CNBu^t$, 7188-38-7.

Supplementary Material Available: Tables of crystal and refinement data, important bond distances and angles, fractional coordinates, and thermal parameters for **4** (Tables S1–S4) and a table listing analytical and complete characterization data for all new compounds reported in this paper (Table S6) (11 pages); a table of structure factors for **4** (Table S5) (60 pages). Ordering information is given on any current masthead page.

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[13] Selected analytical and spectroscopic data for **6** are as follows: IR (Nujol mull) 1500 (s) cm^{-1} (ν(C=N)); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ −21.2 and −16.7 (AB spin system, $^2J_{PP}$ = 284 Hz, 2 trans-PMe_3), −13.8 (s, 1 PMe_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 18.0 (d, $^2J_{CP}$ = 25, $^1J_{CH}$ = 140 Hz, Ni–CH_2), 204.4 (t, $^2J_{CP}$ = 27 Hz, Ni–C=N–). Anal. Calcd for **6**: C, 32.7; H, 5.3. Found: C, 32.6; H, 5.3.

[14] In contrast to CO insertion, CNR insertion into M–C bonds is usually an irreversible process. See, however: Bellachiona, G.; Cardaci, G.; Zanazzi, P. *Inorg. Chem.* **1987**, *26*, 84. Interestingly, nickel complexes frequently induce multiple insertion or even polymerization of iscyanides. See: (a) Otsuka, S.; Nakamura, A.; Yoshida, T.; Naruto, M.; Ataka, K. *J. Am. Chem. Soc.* **1973**, *95*, 3180. (b) Carmona, E.; Marín, J. M.; Palma, P.; Poveda, M. L. *J. Organomet. Chem.* **1989**, *377*, 157.

[15] Through a solution of complex **4** (0.73 g, 1 mmol) in 40 mL of acetone, carbon monoxide was bubbled at room temperature for 5 min. After evaporation of the volatiles under reduced pressure the residue was extracted with Et_2O–CH_2Cl_2. Filtration, concentration, and cooling at −30 °C afforded complex **7** in low yields (25% yield). Representative data for **7**: IR (Nujol mull) 1620 (s) cm^{-1} (ν(C=O)); ^1H NMR (CD_2Cl_2, 20 °C) δ 6.20 (t, $^4J_{HP}$ = 1.9 Hz, HC=CNi); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ −15.6 s; $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 115.4 (t, $^3J_{CP}$ = 7, $^1J_{CH}$ = 163 Hz, Ni–C=*C*H–), 155.3 (t, $^3J_{CP}$ = 37 Hz, Ni–*C*=CH–), 163.1 (s, C=O). Anal. Calcd for **7**: C, 51.2; H, 5.9; N, 2.6. Found: C, 50.8; H, 6.0; N, 2.4.

[16] Intramolecular coupling of acyl and iminoacyl functionalities with formation of C–C bonds has been reported; see: Chamberlan, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L. M.; Latesky, S. L.; McMullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6068.

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Attempted Generation of $Cp(CO)_2Re(\mu\text{-}H)Pt(PPh_3)_2[C(CH_3)=CHCH_3]$ from Reaction of $Cp(CO)_2ReH^-$ with $(PPh_3)_3Pt[(E)\text{-}C(CH_3)=CHCH_3]^+$ Produces $Cp(CO)_2Re(cis\text{-}CH_3CH=CHCH_3)$

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Summary: Previously we proposed $Cp(CO)_2Re(\mu\text{-}H)Pt(PPh_3)_2[C(CH_3)=CHCH_3]$ (**II**) as a possible intermediate in the reaction of 2-butyne with $Cp(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ (**1**) to give $Cp(CO)_2Re(cis\text{-}CH_3CH=CHCH_3)$ (*cis*-**2**). In an attempt to independently synthesize **II**, the reaction of $K^+Cp(CO)_2ReH^-$ (**3**) with $(PPh_3)_3Pt[(E)\text{-}C(CH_3)=CHCH_3]^+CF_3SO_3^-$ (*cis*-**4**) was studied and conversion to *cis*-**2** was observed, but intermediate **II** was not detected. The reaction is stereospecific: *trans*-**4** reacted with **3** to produce *trans*-**2**. $K^+Cp(CO)_2ReD^-$ (**3**-*d*) reacted with *trans*-$Pt[C(CH_3)=CH_2](CF_3SO_3)(PPh_3)_2$ (**5**) to give $Cp(CO)_2Re(CH_2=CDCH_3)$ (**6**-*d*), which demonstrated that **3** is the hydride source in these reactions.

Heterobimetallic compounds hold great promise as catalysts, since the two different metals have the potential of acting cooperatively. During our exploration of new heterobimetallic compounds and their reactions with organic substrates, we discovered that the rhenium–platinum dihydride $(C_5H_5)(CO)_2Re(\mu\text{-}H)Pt(H)(PPh_3)_2$ (**1**)[1] reacted with alkyl-substituted alkynes to give *cis*-(alkene)rhenium complexes. We also found that **1** catalyzed the reaction of $CpRe(CO)_2H_2$ with alkynes to give rhenium alkene complexes in high yields.[2]

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[1] Casey, C. P.; Rutter, E. W., Jr.; Haller, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 6886.

[2] Casey, C. P.; Rutter, E. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 8917.

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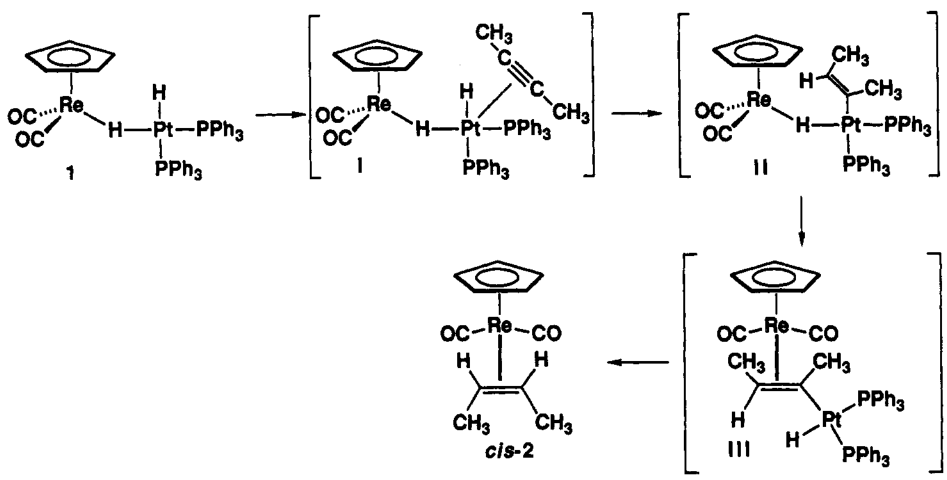
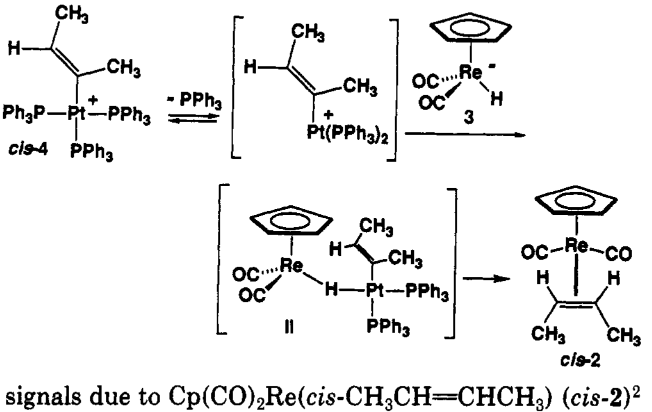
Scheme I



Since reductions by authentic heterobimetallic systems are rare and potentially very important, we are investigating the mechanism of these reactions in detail. Our initial mechanistic hypothesis for the reduction of 2-butyne to $Cp(CO)_2Re(\textit{cis}\text{-}CH_3CH{=}CHCH_3)$ (*cis*-**2**) is shown in Scheme I. Reactions analogous to the addition of a platinum hydride across the complexed alkyne to produce the vinylplatinum compound II are well documented.[3] For example, cis addition of *trans*-$PtH(PEt_3)_2(acetone)^+$ to $CH_3C{\equiv}CCH_3$ produced *trans*-$Pt(py)(PEt_3)_2[C(CH_3){=}CHCH_3]^+$.[3b] Complexes such as $[(Ph_3P)_2(CO)Ir(\mu\text{-}H)(\mu\text{-}\eta^2{:}\eta^1\text{-}CH{=}CH_2)Pt(PPh_3)_2]^+CF_3SO_3^-$ with (π-vinyl)M, (σ-vinyl)M′ bonds similar to those in III have been observed.[4]

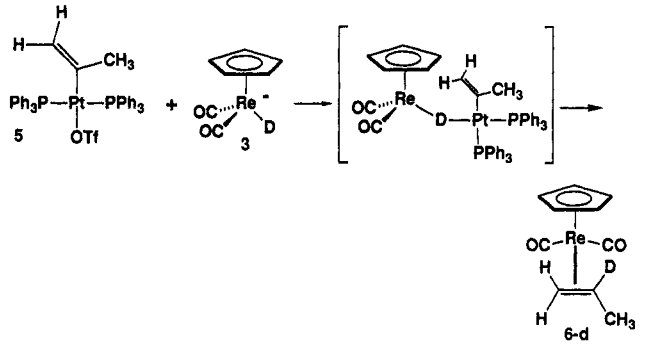
In an attempt to generate the proposed rhenium platinum vinyl intermediate II, the reaction of $K^+Cp(CO)_2ReH^-$ (**3**)[5] with 1 equiv of $(PPh_3)_3Pt[(E)\text{-}C(CH_3){=}CHCH_3]^+CF_3SO_3^-$ (*cis*-**4**)[6] in CD_3CN at 17 °C was monitored by ^1H NMR spectroscopy. During the reaction, signals due to $Cp(CO)_2Re(\textit{cis}\text{-}CH_3CH{=}CHCH_3)$ (*cis*-**2**)[2] gradually grew in over several hours and $Pt(PPh_3)_3$ precipitated as a yellow solid. The reaction was extremely clean: a 101 ± 3% yield of *cis*-**2** was measured by ^1H NMR spectroscopy using mesitylene as an internal standard. In a preparative reaction, an acetonitrile solution of **3** (14 mg, 40 μmol) and *cis*-**4** (33 mg, 28 μmol) was stirred for 3 h at room temperature, decanted from precipitated $Pt(PPh_3)_3$, and evaporated to dryness. *cis*-**2** (10 mg, 27 μmol, 98%) was isolated by preparative thin-layer chromatography (silica gel, 1:9 CH_2Cl_2:hexane).



Similarly, reaction of **3** with 1 equiv of an 89:11 mixture of $(PPh_3)_3Pt[(Z)\text{-}C(CH_3){=}CHCH_3]^+CF_3SO_3^-$ (*trans*-**4**)[6] and *cis*-**4** in CD_3CN at 17 °C produced an 87:13 mixture of $CpRe(CO)_2(\textit{trans}\text{-}CH_3CH{=}CHCH_3)$ (*trans*-**2**)[7] and *cis*-**2** as shown by ^1H NMR spectroscopy. The reaction of *trans*-**4** was about 8 times faster than that of *cis*-**4** but occurred with a lower yield of *trans*-**4** (60% yield by NMR, 31% isolated yield). These results indicate that the conversion of **4** to **2** occurs stereospecifically with retention of stereochemistry.

The kinetics of the reaction of *cis*-**4** with excess **3** was studied in CD_3CN at 25 °C. The reaction was first order in vinylplatinum compound *cis*-**4** and zero order in rhenium hydride **3**.[8] This suggests that phosphine dissociation is the rate-determining step.

The reaction of the covalent triflate *trans*-$Pt[C(CH_3){=}CH_2](CF_3SO_3)(PPh_3)_2$ (**5**)[6] with **3** in THF-d_8 was followed by ^1H NMR spectroscopy. After 15 min, analysis of the dark red solution indicated that $Cp(CO)_2Re(CH_2{=}CHCH_3)$ (**6**;[2] 66%) was the major product; in addition, small Cp signals due to $CpRe(CO)_2PPh_3$ (10%), **3** (13%), and **1** (8%) were observed. When the reaction was performed under ethylene, the solution remained yellow and a 1:1 mixture of **6** and $Ph(PPh_3)_2(C_2H_4)$ was observed by ^1H NMR spectroscopy.



To establish the fate of the hydride ligand in these reactions, the reaction of $K^+CpRe(CO)_2D^-$ (**3**-*d*; prepared

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[8] The reaction of *cis*-**4** (0.01 M) with excess **3** in CD_3CN at 25 °C followed pseudo-first-order kinetics to over 4 half-lives. The pseudo-first-order rate constants for [**3**] = 0.044 and 0.095 M were (6.37 ± 0.16) × 10^{-4} and (6.57 ± 0.32) × 10^{-4} s^{-1}.

from >95% $CpRe(CO)_2D_2$ and KH) with **5** in THF was followed by ^{2}H NMR spectroscopy. Only one signal at δ 4.05 due to $Cp(CO)_2Re(CH_2{=}CDCH_3)$ (**6-*d***) was detected.

We have attempted to independently synthesize the intermediate II proposed for alkyne hydrogenation by Re–Pt dihydride **1**. Although II was not observed, the risky prediction of Re alkene complex formation with retention of vinyl stereochemistry was borne out, consistent with our hypothesis that II is a precursor of rhenium alkene complexes. The reactions of vinylplatinum compounds with $Cp(CO)_2ReH^-$ (**3**) are rare examples of the cleavage of a vinyl–transition-metal bond by a transition-metal hydride.[9]

Acknowledgment. Financial support from the Department of Energy, Division of Basic Energy Sciences, is gratefully acknowledged. We thank Johnson-Matthey for a generous loan of precious metals.

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[9] For other examples of reactions of MR with M'H which produce RH, see: (a) Ruszczyk, R. J.; Huang, B.-L.; Atwood, J. D. *J. Organomet. Chem.* **1986**, *299*, 205. (b) Bartik, T.; Happ, B.; Sorkau, A.; Thiele, K.-H.; Palyi, G. *Organometallics* **1989**, *8*, 558. (c) Nappa, M. J.; Santi, R.; Halpern, J. *Organometallics* **1985**, *4*, 34. (d) Hoxmeier, R. J.; Blickensderfer, J. R.; Kaesz, H. D. *Inorg. Chem.* **1979**, *18*, 3453. (e) Hoxmeier, R. J.; Knobler, C. B.; Kaesz, H. D. *Inorg. Chem.* **1979**, *18*, 3462. (f) Edidin, R. T.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 948. (g) Renaut, P.; Tainturier, G.; Gautheron, B. *J. Organomet. Chem.* **1978**, *150*, C9.

[3 + 1] Cycloaddition: Reaction of Dichlorogermylene with Hexafluoro-2-propanethione 1-Adamantylimide

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Summary: Reaction of hexafluoro-2-propanethione 1-adamantylimide (**1**) and dichlorogermylene at room temperature gives the [3 + 1] cycloadduct $(CF_3)_2CSN(R)GeCl_2$ (**2**; R = adamantyl). The bond angles of the four-membered CSNGe heterocycle **2** are all close to 90°. This compound exhibits an unexpected stability at room temperature.

Cycloaddition reactions play an important role in organic chemistry, but only a few publications have appeared that deal with [3 + 1] cycloaddition reactions.[1-6] To our knowledge, there have so far been no reports on [3 + 1] cycloaddition reactions with carbenes or their homologues.[7] Heterocumulenes are important precursors for cycloaddition reactions.[8]

Recently we described the synthesis of $(CF_3)_2C{=}S{=}NR$ (**1**; R = 1-adamantyl) using $Cl(CF_3)_2CSN(H)R$ as starting material.[9] The latter compound reacts with $NaN(SiMe_3)_2$ or $LiN(SiMe_3)_2$ in a 1,3-dehydrochlorination reaction to yield **1**. We have shown that **1** reacts with norbornene in a [2 + 3] cycloaddition reaction to yield the isothiazolidine.[9]

Herein we describe the reaction of **1** with dichlorogermylene–dioxane to yield $(CF_3)_2CSN(R)GeCl_2$ (**2**).

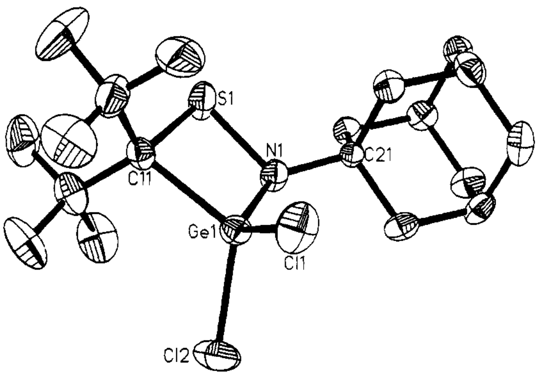
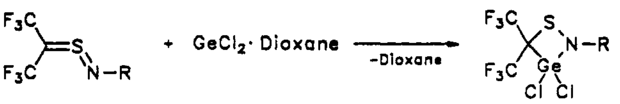


Figure 1. Structure of **2**, shown with 50% thermal ellipsoids. Selected bond distances (Å) and angles (deg) are as follows: Ge1–N1 = 1.813 (3), Ge1–Cl1 = 2.008 (4), N1–S1 = 1.787 (4), S1–C11 = 1.819 (4); N1–Ge1–Cl1 = 82.9 (2), Ge1–N1–S1 = 96.9 (2), N1–S1–C11 = 89.3 (2), S1–C11–Ge1 = 89.4 (2).

Scheme I



1 2

R= 1-Adamantyl-

The reaction of **1** with 1 molar equiv of dichlorogermylene–dioxane in Et_2O at 20 °C afforded **2** (mp 103 °C) in 42% yield. After recrystallization from THF at −20 °C, yellow crystals of **2** are obtained that hydrolyze readily when exposed to air. In the ^{19}F NMR spectrum of **2** a single line at −62.3 ppm is consistent with formation of the four-membered heterocyclic cycloaddition product. This has been confirmed by the single-crystal X-ray structure[10] (Figure 1).

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[5] Deyrup, J. A. *Tetrahedron Lett.* **1971**, 2191.

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[7] A 1,3-cycloaddition intermediate has been observed as an intermediate in the reaction of a germylene with a nitrone but not isolated: Rivière, P.; Satgé, J.; Castel, A.; Cazes, A. *J. Organomet. Chem.* **1979**, *177*, 171.

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[9] May, A.; Roesky, H. W.; Stalke, D.; Pauer, F.; Sheldrick, G. M, *Chem. Ber.* **1990**, *123*, 1475.

[10] Crystal data for $C_{13}H_{15}Cl_2F_6GeNS$ (**2**) at −120 °C: $a = 11.811$ (2) Å, $b = 11.431$ (2) Å, $c = 12.800$ (2) Å, $\beta = 91.42$ (2)°, $V = 1727.6$ (5) Å^3, $Z = 4$, $d_{calcd} = 1.83$ g/cm^3, space group $P2_1/c$. A total of 2661 reflections were measured on a STOE-Siemens-AED diffractometer. After equivalent reflections were merged, 1937 reflections with $F > 3\sigma(F)$ were used for all calculations (all programs written by G.M.S.): final residual $R = 0.039$, $R_w = 0.033$. A riding model with idealized hydrogen geometry was employed for H atom refinement. Further details of the structure determination (atomic coordinates, complete bond lengths and angles, structure factors, and displacement parameters) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote the full literature citation and the reference number (CSD 55654).

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