Binuclear Complexes of Nickel Bridged by Hydrocarbon Ligands. Isocyanide Insertion Chemistry and Amide Formation by Intramolecular Coupling of Acyl and Imidoyl Functionalities

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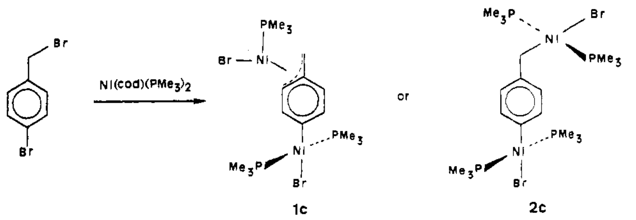
Summary: Ni(cod)(PMe$_3$)$_2$ and the *o*-, *m*-, and *p*-bromobenzyl bromides react, under appropriate conditions, to afford the binuclear complexes Ni$_2$(μ_2-η^3,η^1-CH$_2$C$_6$H$_4$)Br$_2$(PMe$_3$)$_3$ (**1a–c**) or Ni$_2$(μ_2-η^1,η^1-CH$_2$C$_6$H$_4$)Br$_2$(PMe$_3$)$_4$ (**2b,c**). The reaction of the ortho η^3-benzylic derivative **1a** with isocyanides, CNR, has been investigated, and three different isomeric species have been identified for R = Bu^t. The CNC$_6$H$_3$-2,6-Me$_2$ insertion product, **4**, reacts with CO to form a Ni(II)-vinyl complex **7** derived from the *N*-aryl-1-isoquinolone **8**, which can be freed by hydrolytic cleavage of the Ni–vinyl bond.

Binuclear transition-metal complexes bridged by hydrocarbon ligands have attracted considerable attention in recent years.[1] This is due both to their structural interest and to the possibility of observing new useful transformations by means of the cooperative effects between the two potentially reactive metal centers. Following our recent studies on the chemical reactivity of the Ni–C bonds in complexes of the strongly basic PMe$_3$ ligand,[2] we have prepared binuclear complexes containing Ni–CH$_2$Ar and Ni–Ar functionalities (Ar = aryl group) and studied their chemical behavior. Here we report preliminary results obtained with the *o*-, *m*-, and *p*-CH$_2$C$_6$H$_4$ biradicals, which include the synthesis of the corresponding binuclear complexes (**1a–c** and **2b,c**; Scheme I) as well as some reactivity studies, in particular their reactions toward isocyanides (Scheme II). Formation of amide derivatives by intramolecular coupling of an acyl and an imidoyl functionality is also described.

The oxidative addition reaction of Ni(cod)(PMe$_3$)$_2$ and the *o*-, *m*-, and *p*-bromobenzyl bromides, BrCH$_2$C$_6$H$_4$Br, gives, under appropriate conditions,[3] compounds **1a–c** or **2b,c** (Scheme I). Interestingly, the ortho derivative **1a** is so prone to adopt the pseudoallylic structure[4] that the corresponding η^1-benzylic derivative **2a** cannot be isolated in the solid state.

Scheme I. Synthesis of Binuclear η^1- and η^3-Benzyl Complexes of Nickel[a]



[a] Starting with *m*-BrCH$_2$C$_6$H$_4$Br, the corresponding compounds **1b** and **2b** are obtained, while for *o*-BrCH$_2$C$_6$H$_4$Br only **1a** can be isolated in the solid state.

Compound **1a**,[5] in which the proximity effects of the two metal centers are expected to be maximized, exhibits the most interesting reactivity (Scheme II). Interaction with the bidentate, small bite-angle, Me$_2$PCH$_2$PMe$_2$ ligand gives the binuclear complex **3**.[6] Isocyanides insert readily and selectively into the Ni–benzylic bond. For example, reaction with 2,6-dimethylphenyl isocyanide (CNXy) provides complex **4** for which spectroscopic data suggest a μ_2-imidoyl formulation.[7] Since this is a rather unusual binding mode for imidoyl ligands,[8] an X-ray structural

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(1) (a) Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. J. W. *Chem. Rev.* **1983**, *83*, 135. (b) Moss, J. R.; Scott, L. G. *Coord. Chem. Rev.* **1984**, *60*, 171. (c) Casey, C. P.; Andett, J. D. *Chem. Rev.* **1986**, *86*, 339.

(2) (a) Carmona, E.; Gutiérrez-Puebla, E.; Monge, A.; Marín, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1989**, *8*, 967. (b) Carmona, E.; Gutiérrez-Puebla, E.; Marín, J. M.; Monge, A.; Paneque, M.; Poveda, M. L.; Ruiz, C. *J. Am. Chem. Soc.* **1989**, *111*, 2883. (c) Carmona, E.; Palma, P.; Paneque, M.; Poveda, M. L. *Organometallics* **1990**, *9*, 583.

(3) The oxidative-addition reaction occurs in a step-wise manner and yields first the mononuclear complexes *o*-, *m*-, or *p*-BrC$_6$H$_4$CH$_2$NiBr(PMe$_3$)$_2$, clearly reflecting the greater reactivity of the benzylic functionality. Interaction with another 1 equiv of Ni(cod)$_2$ affords the binuclear derivatives **1a–c** or **2b,c**, depending on the amount of PMe$_3$ present in the reaction mixture.

(4) For recent examples of η^3-benzylic complexes of Ni, see: (a) Carmona, E.; Marín, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1987**, *6*, 1757. (b) Lehmkuhl, H.; Keil, T.; Benn, R.; Rufińska, A.; Krüger, C.; Poplawska, J.; Bellenbaum, M. *Chem. Ber.* **1988**, *121*, 1931. (c) Carmona, E.; Paneque, M.; Poveda, M. L. *Polyhedron* **1989**, *8*, 285.

(5) To a stirred suspension of Ni(cod)$_2$ (1.1 g, 4 mmol) in Et$_2$O (80 mL) was added 0.6 mL of PMe$_3$ (6 mmol). After the mixture was stirred for 2–3 h at room temperature, the stirring was discontinued, 2 mL of a 1 M toluene solution of BrCH$_2$C$_6$H$_4$-*o*-Br slowly introduced, and the resulting mixture left undisturbed for a few hours. The precipitated red-orange crystals of **1a** were collected and dried in vacuo (60–70% yield). From the mother liquor an additional crop (10–20% yield) was obtained. Analytical and selected spectroscopic data for **1a** are as follows: ^{31}P{^{1}H} NMR (81 MHz, CD$_2$Cl$_2$, −70 °C) δ −12.8 and −7.4 (AB spin system, $^2J_{PP}$ = 398 Hz, 2 trans-PMe$_3$), −5.0 (s, 1 PMe$_3$); ^{13}C{^{1}H} NMR (50 MHz, CD$_2$Cl$_2$, −70 °C) δ 30.5 (d, $^2J_{CP}$ = 8, $^1J_{CH}$ = 152 Hz, Ni–CH$_2$), 105.1 (d, $^2J_{CP}$ = 11 Hz, Ni–C$_{ar}$H), 119.9 (d, $^2J_{CP}$ = 6 Hz, Ni–C$_{ar}$), 166.5 (t, $^2J_{CP}$ = 34 Hz, Ni–C$_{ar}$). Anal. Calcd for **1a**: C, 32.2; H, 5.5. Found: C, 31.8; H, 5.5.

(6) Representative analytical and spectroscopic data for **3**: ^{31}P{^{1}H} NMR (CD$_3$COCD$_3$, 20 °C) (AA′BB′ spin system) δ_A −4.5, δ_B −3.8, $J_{AA'} \simeq J_{BB'}$ = 450, J_{AB} = 58, $J_{AB'}$ = 2 Hz; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 20 °C) δ 13.1–16.9 (complex multiplets, P–Me and Ni–CH$_2$), 30.0 (pseudoquintet, $J_{CP_{app}}$ = 11 Hz, PCH$_2$P), 156.0 (t, $^2J_{CP}$ = 29 Hz, Ni–C$_{ar}$). Anal. Calcd for **3**: C, 32.1; H, 4.7. Found: C, 31.2; H, 5.0.

(7) A cold (−60 °C) stirred solution of **1a** (0.60 g, 1 mmol) in 40 mL of THF was treated with 0.13 g (1 mmol) of CNXy dissolved in 10 mL of THF. The cooling bath was removed and the solvent stripped off at room temperature. Extraction with 100 mL of Et$_2$O, filtration, concentration, and cooling at −30 °C furnished complex **4** as a crystalline material (65% yield). ν(C=N) and δ(Ni–*C*(=NR)–) for the imidoyl functionality in **4** appear at ca. 1495 cm^{-1} and 224 ppm, respectively. These values are appreciably different from those characteristic of well-characterized mononuclear η^1- and η^2-imidoyl complexes of Ni.[2c] Other relevant analytical and spectroscopic data are as follows: ^{1}H NMR (200 MHz, CD$_3$COCD$_3$, 20 °C) δ 5.02 and 5.47 (AB spin system, $^2J_{HH}$ = 16 Hz, CH$_2$); ^{31}P{^{1}H} NMR (CD$_3$COCD$_3$, 20 °C) δ −15.4 and −8.1 (AB spin system, $^2J_{PP}$ = 267 Hz, 2 trans-PMe$_3$), −7.0 (s, 1 PMe$_3$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 20 °C) δ 58.9 (d, J_{CP} = 12, $^1J_{CH}$ = 128 Hz, CH$_2$), 153.6 (d, $^2J_{CP}$ = 44 Hz, Ni–C$_{ar}$), 224.2 (t, $^2J_{CP}$ = 27 Hz, Ni–C=N–). Anal. Calcd for **4**: C, 41.0; H, 5.7; N, 1.9. Found: C, 41.0; H, 5.9; N, 1.5.

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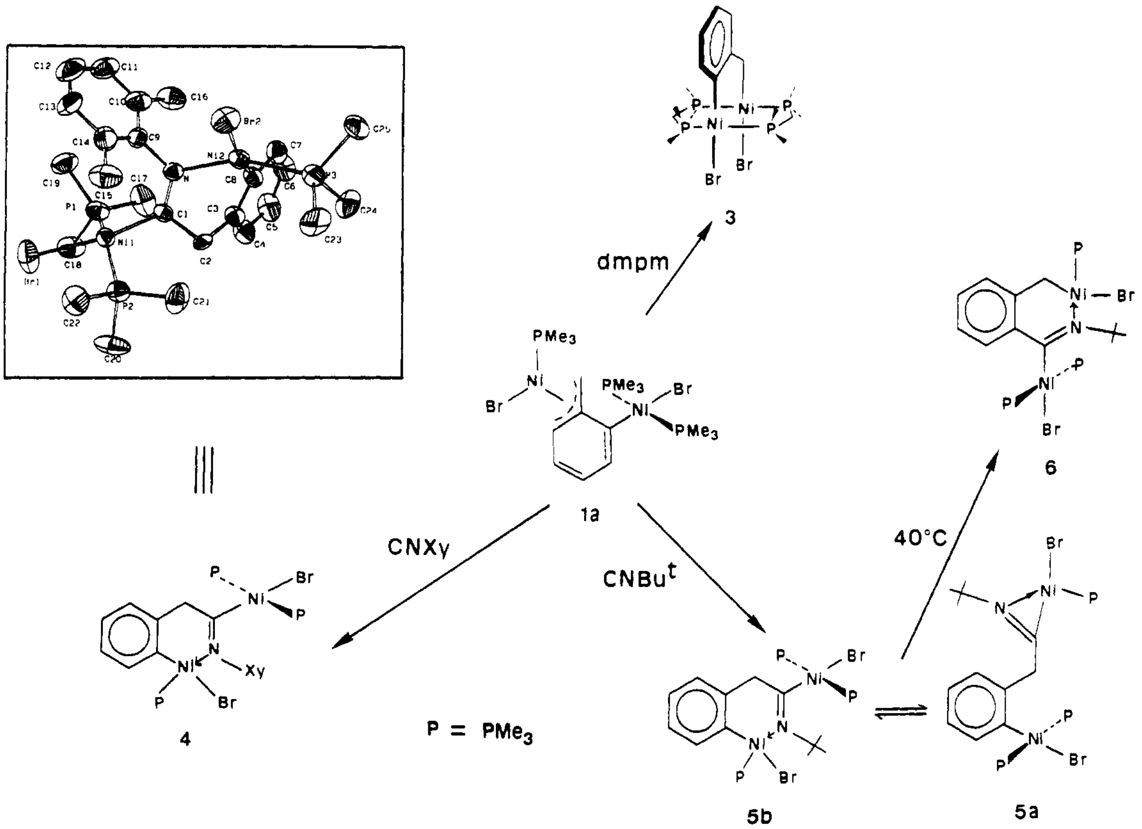
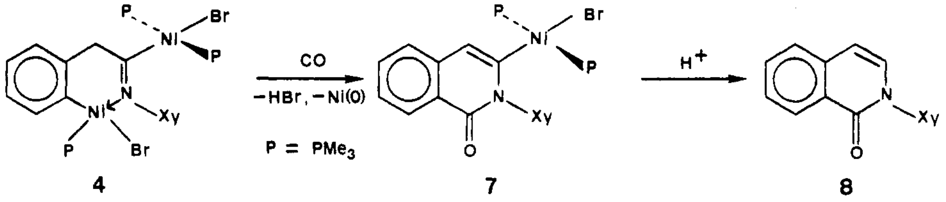
Scheme II



Scheme III



investigation was undertaken.[9]

A somewhat more complex reaction takes place in the presence of CNBu^t. As shown in Scheme II, this provides (20 °C) a thermodynamic mixture of two isomers, **5a** and **5b**, both resulting from the insertion of the isocyanide into the Ni–benzylic bond. Of these, **5b** is structurally related[10] to the μ_2-imidoyl complex **4** described above, while for isomer **5a** spectroscopic data indicate an open structure in which the imidoyl functionality is η^2-bonded to the metal center.[11]

Interestingly, the position of the **5a** $\rightleftharpoons$ **5b** equilibrium is dramatically solvent dependent. Thus, both species have almost identical stability in THF (K_{eq} = [**5a**]/[**5b**] $\simeq$ 1), while in CH_2Cl_2 and CH_3COCH_3 the open structure **5a** is strongly favored ($K_{eq} \simeq 6$). It is also worth pointing out that the reaction of **1a** with CNBu^t in THF at −80 °C yields exclusively isomer **5a** with the equilibrium **5a** $\rightleftharpoons$ **5b** being only established at temperatures above −20 °C. Crystallization of **5a** $\rightleftharpoons$ **5b** mixtures from Et_2O provides crystalline samples of **5b**.[12]

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(8) (a) Usón, R.; Forniés, J.; Espinet, P.; Lalinde, E.; García, A.; Jones, P. G.; Meyer-Bäse, K.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1986**, 259. (b) Seyferth, D., Hoke, J. B. *Organometallics* **1988**, *7*, 524. (c) Bertani, R.; Berton, A.; Di Bianca, F.; Crociani, B. *J. Organomet. Chem.* **1988**, *348*, 411.

(9) Crystal data for **4**, $C_{25}H_{42}NP_3Br_2Ni_2$: monoclinic, $P2_1/n$, a = 12.437 (3) Å, b = 16.025 (2) Å, c = 16.015 (2) Å, β = 101.47 (1)°, V = 3128.1 (9) Å^3, Z = 4, D(calcd) = 1.54 g cm^{-3}, λ(Mo Kα) = 0.71069 Å (graphite monochromator), T = 22 °C. A summary of the fundamental crystal data is given in Table S1 (supplementary material). An orange crystal (0.2 × 0.4 × 0.3 mm) was coated in epoxy resin to prevent crystal decay and mounted on a κ–geometry diffractometer. The cell dimensions were refined by least-squares fitting the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ni, Br, and P were taken from: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; pp 72–98. The structure was solved by Patterson and Fourier methods. An empirical absorption correction (Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *A39*, 158) was applied at the end of the isotropic refinement. Final refinement was with fixed isotropic factors for H atoms. R = 0.052 and R_W = 0.057. Most of the calculations were carried out with the X-RAY 80 system: Stewart, J. M. Computer Science Center, University of Maryland, College Park, MD, 1985.

(10) Compound **5b** has been structurally characterized by X-ray studies to be reported separately.

(11) Selected spectroscopic data for **5a**: IR (CD_2Cl_2 solution) 1730 (s) cm^{-1} (ν(C═N)); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −70 °C) δ −9.2 (s, 2 PMe_2), −1.5 (s, 1 PMe_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 20 °C) δ 36.8 (s, $^1J_{CH}$ = 129 Hz, CH_2), 158.2 (t, $^2J_{CP}$ = 34 Hz, Ni–C_{ar}), 169.2 (s, C═N, a fast phosphine exchange process probably cancels the expected coupling with the cisoid phosphorus nucleus).

(12) As shown in Scheme II, complex **4** exists exclusively in solution in the "close" μ_2-imidoyl form, even in CH_2Cl_2 solution. Monitoring the reaction of **1a** with CNXy by $^{31}P\{^1H\}$ NMR spectroscopy (CD_2Cl_2, −60 °C to room temperature) shows the formation of **4** with no detectable intermediates. It seems reasonable that an "open" structure, analogous to **5a**, is formed in this reaction but converts readily, even at very low temperatures, into the more thermodynamically stable μ_2-imidoyl structure. The different behaviors of the two isocyanides may be a reflection of their steric requirements. The importance of the steric bulkiness of the isocyanide and the coligands in the stabilization of the η^2-alkaneimidoyl structure in complexes of nickel has recently been demonstrated.[2c]

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.; Marin, 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.

[17] Colquhoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. *New Pathways for Organic Synthesis*; Plenum Press: New York, 1984; Chapter 6.

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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