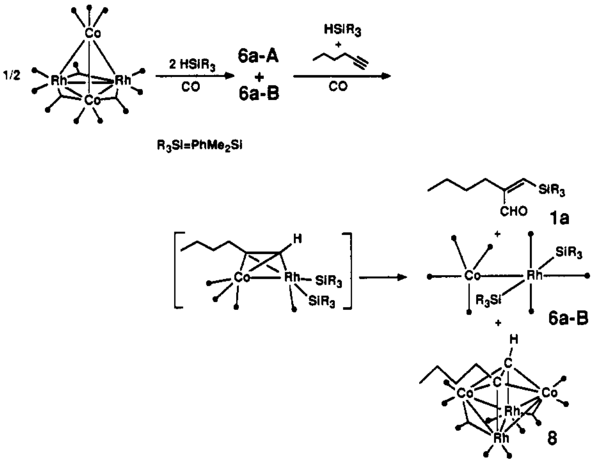
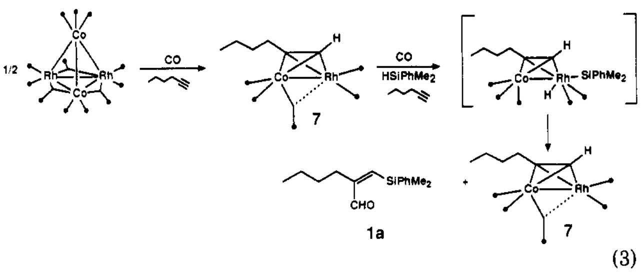


(2)

catalyst species or its direct precursor.

Next, we looked at the reaction of $Co_2Rh_2(CO)_{12}$ with 1-hexyne under carbon monoxide. The reaction of $Co_2Rh_2(CO)_{12}$ with 2 equiv of 1-hexyne at 25 °C and 75 psi of carbon monoxide in hexane for 6 h gave a novel Rh–Co mixed bimetallic alkyne complex bearing a semibridging carbonyl (ν_{CO} 1935 cm^{-1}), RhCo(n-Bu-C≡CH)$(CO)_5$ (7), as the major product, which was isolated through column chromatography on silica gel under carbon monoxide as a reddish orange solid.[15] Complex **7** was then allowed to react with 6 equiv of dimethylphenylsilane and 4 equiv of 1-hexyne at 25 °C and ambient pressure of carbon monoxide in chloroform for 1 h to give cleanly the silylformylation product **1a**; viz., the ^1H NMR spectrum of the reaction mixture only shows **1a**, **7**, and unreacted hydrosilane (eq 3). This result clearly indicates that **7** is an active catalyst species or its direct precursor.

Accordingly, there are two possible catalytic cycles for silylformylation at present, and either one or both catalytic cycles may be operative depending on the reaction conditions. Mechanisms for the silylformylation of 1-hexyne



(3)

with $Co_2Rh_2(CO)_{12}$ as the catalyst precursor, which can accommodate all the observations described above, are proposed in Scheme I.

It should be noted that the unique bis(silyl)–RhCO complex **6** and alkyne–RhCo complex **7** are indentified as the key catalytic species for silylformylation of a 1-alkyne. Although the insertion of carbonyl compounds or imines into silicon–transition-metal bonds is known in rhodium-complex-catalyzed hydrosilylations, that of alkynes and alkenes in catalysis has not been reported under thermal reaction conditions.[16] Our results present the first examples of such a process in catalysis by taking advantage of the unique properties of the Co–Rh mixed bimetallic system. Also, it is noteworthy that the silylformylation of alkynes catalyzed by Co–Rh mixed-metal systems is very likely to involve "*homogeneous bimetallic catalysis*".

Further study on the mechanism and applications of silylformylation promoted by Rh–Co mixed-metal catalysts is actively underway.

Acknowledgment. This work has been supported by grants from the National Science Foundation, the National Institutes of Health (NIGMS), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Mitsubishi Kasei Corp.

Supplementary Material Available: Typical procedures for eqs 1–3, identification data for silylformylation products **1**, and ^1H spectra of the reaction mixtures for eqs 2 and 3 (3 pages). Ordering information is given on any current masthead page.

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[15] **7**: orange solid; FT-IR (hexane) 2076 m, 2058 s, 2018 vs, 1934 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (m, 3 H), 1.10–1.85 (m, 4 H), 2.38 (m, 1 H), 3.23 (m, 1 H), 5.64 (s, 1 H); ^{13}C NMR δ 13.8, 22.4, 34.1, 42.0, 93.4 (m, ≡CH), 167.5 (≡CBu^n), 175.8 (d, J = 32.7 Hz, Rh–CO), 178.2 (d, J = 83.9 Hz, Rh–CO), 203 (br). Anal. C, H.

[16] Recently, we found the selective insertion of 1-alkynes into an Rh–Si bond in rhodium-complex-catalyzed hydrosilylation. See: Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics*, in press.

Ruthenium Amine and Amide η^5-Cyclopentadienyl Complexes Having Monodentate Phosphines, Phosphites, or 1,2-Bis(dicyclohexylphosphino)ethane as Supporting Ligands

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Summary: Reacting $(\eta^5\text{-cp})RuCl(PPh_3)_2$ with $Cy_2PCH_2CH_2PCy_2$ and then $AgCF_3SO_3$ and ammonia gives $[(\eta^5\text{-cp})Ru(NH_3)(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$, which reacts with H^- to give $(\eta^5\text{-cp})Ru(NH_2)(Cy_2PCH_2CH_2PCy_2)$. Similar synthetic strategies have been used to prepare $[(\eta^5\text{-cp})Ru(NH_3)(PPh_3)_2]CF_3SO_3$, $[(\eta^5\text{-cp})Ru(NH_2CMe_3)(PPh_3)(P(OMe)_3)]CF_3SO_3$, and $[(\eta^5\text{-cp})Ru(NH_2Me)(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$, the first two of which have been confirmed by X-ray crystallography.

Monomeric organotransition-metal compounds containing a terminal unsubstituted NH_2 ligand are uncommon.[1] One reason for this scarcity is the ease with which such complexes undergo substitution oligomerization with

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[1] For example see: Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1–40. Bryndza, H. E.; Tam, W. *Chem. Rev.* **1988**, *88*, 1163–1188. Park, S.; Roundhill, D. M.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 3972–3974. Hillhouse, G. L.; Bulls, A. R.; Santarsiero, B. D.; Bercaw, J. E. *Organometallics* **1988**, *7*, 1309–1312.

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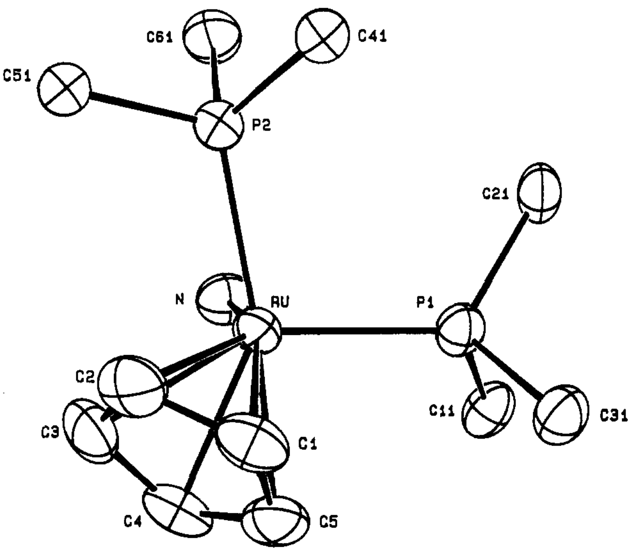

Figure 1. ORTEP diagram of $[(\eta^5\text{-cp})Ru(NH_3)(PPh_3)_2]^+$. For clarity only the ipso phenyl carbons are shown. Selected bond distances (Å) and angles (deg): Ru-P(1) = 2.3533 (9), Ru-P(2) = 2.3463 (9), Ru-N = 2.172 (3), Ru-C(1) = 2.203, Ru-C(2) = 2.178 (4), Ru-C(3) = 2.193 (4), Ru-C(4) = 2.208 (4), Ru-C(5) = 2.212 (4); P(1)-Ru-P(2) = 102.29 (3), P(1)-Ru-N = 90.41 (8), P(2)-Ru-N = 89.67 (8).

the formation of amide bridges.[2] Monomeric organometallic amide complexes are of interest, however, because they offer an entry into organotransition-metal heteroatom chemistry by allowing the reactivity of a coordinated amide to be studied. Such complexes can be synthesized either by the deprotonation of a complexed amine or by the metathetical replacement of an anionic ligand by amide ion. Our strategy to inhibit substitution oligomerization involves the use of sterically bulky chelating ligands.

When a solution of $(\eta^5\text{-cp})RuCl(PPh_3)_2$ and $Cy_2PCH_2CH_2PCy_2$ is refluxed in benzene, the complex $(\eta^5\text{-cp})RuCl(Cy_2PCH_2CH_2PCy_2)$ if formed in high yield.[3] Treating a THF solution of this complex with silver triflate and then with excess ammonia gives the cationic amine complex $[(\eta^5\text{-cp})Ru(NH_3)(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$ (eq 1).[4] The analogous complex $[(\eta^5\text{-cp})Ru(NH_3)(PPh_3)_2]$-

$$(\eta^5\text{-cp})RuCl(Cy_2PCH_2CH_2PCy_2) + AgCF_3SO_3 \xrightarrow{NH_3} [(\eta^5\text{-cp})Ru(NH_3)(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3 + AgCl \quad (1)$$

CF_3SO_3, prepared similarly from $(\eta^5\text{-cp})RuCl(PPh_3)_2$, silver triflate, and ammonia, has been characterized by X-ray crystallography.[5] An ORTEP representation of the cation is shown in Figure 1. The molecule has a distorted "piano stool" structure with an Ru-N distance of 2.172 (3) Å. This distance is close to the range of Ru-NH_3 distances (2.166 (7)-2.145 (6) Å) found in $[Ru(NH_3)_5pz](BF_4)_2$.[6]

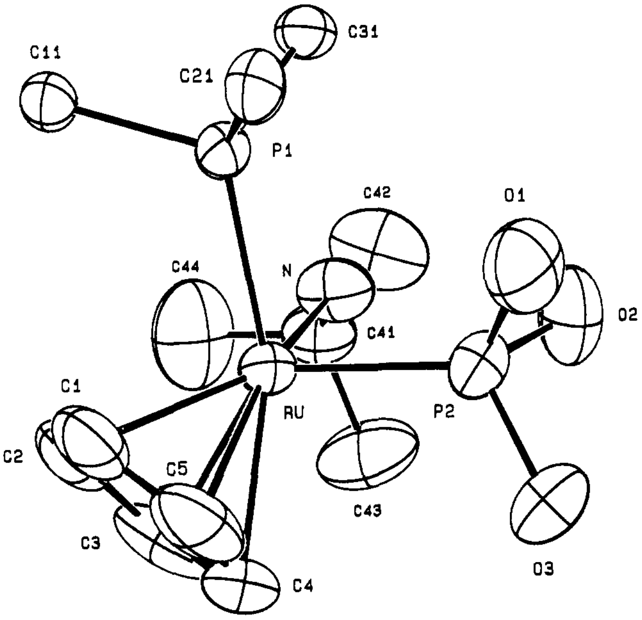

Figure 2. ORTEP diagram of $[(\eta^5\text{-cp})Ru(NH_2CMe_3)(PPh_3)(P(OMe)_3)]^+$. For clarity only the ipso phenyl carbons and phosphite oxygens are shown. Selected bond distances (Å) and angles (deg): Ru-P(1) = 2.3183 (7), Ru-P(2) = 2.2501 (8), Ru-N = 2.216 (2), Ru-C(1) = 2.183 (3), Ru-C(2) = 2.225 (3), Ru-C(3) = 2.229 (3), Ru-C(4) = 2.227 (3), Ru-C(5) = 2.179 (3); P(1)-Ru-P(2) = 93.77 (3), P(1)-Ru-N = 87.65 (7), P(2)-Ru-N = 88.35 (8).

Reacting a THF solution of $[(\eta^5\text{-cp})Ru(NH_3)(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$ with potassium hydride causes deprotonation of the ammine ligand and formation of the neutral amide complex $(\eta^5\text{-cp})Ru(NH_2)(Cy_2PCH_2CH_2PCy_2)$ (eq 2).[7] By ^1H and $^{31}P\{^1H\}$ NMR

$$[(\eta^5\text{-cp})Ru(NH_3)(Cy_2PCH_2CH_2PCy_2)]^+ + H^- \rightarrow (\eta^5\text{-cp})Ru(NH_2)(Cy_2PCH_2CH_2PCy_2) + H_2 \quad (2)$$

spectroscopy, no other ruthenium complexes are present in the clear orange solution. Solvent removal in vacuo gives the compound as an orange/brown hygroscopic solid that is soluble in organic solvents. We believe that this is the first example of an organometallic compound having a Ru-NH_2 linkage. Alternatively, the amide complex can be prepared by reacting sodium amide with $[(\eta^5\text{-cp})Ru(THF)(Cy_2PCH_2CH_2PCy_2)]^+$. By comparison, the monomeric amide product formed from $[(\eta^5\text{-cp})Ru(NH_3)(PPh_3)_2]^+$ and potassium hydride decomposes to several products because of the ready loss of a triphenylphosphine ligand followed by further reactions. The formation of $(\eta^5\text{-cp})Ru(NH_2)(Cy_2PCH_2CH_2PCy_2)$ is verified by the relative intensity of the C_5H_5 and NH_2 resonances in the ^1H NMR spectrum and the high-field shift of the NH_2 hyrogens.[7,9] The NH_2 resonance is upfield-shifted upon dilution, indicative of intermolecular hydrogen bonding in the complex. Furthermore, a THF solution of $(\eta^5\text{-cp})Ru(NH_2)(Cy_2PCH_2CH_2PCy_2)$ reacts with $[Me_4N]BF_4$,

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(2) Casalnuovo, A. L.; Calabrese, J. C.; Milstein, D. *Inorg. Chem.* **1987**, *26*, 973–976. Curtis, N. J.; Hagen, K. S.; Sargeson, A. M. *Inorg. Chem.* **1984**, *23*, 1571–1573. Rotzinger, F. P.; Marty, W. *Inorg. Chem.* **1983**, *22*, 3593–3602. Kretschmer, M.; Heck, L. *Z. Anorg. Allg. Chem.* **1982**, *490*, 215–229. Alcock, N. W.; Bergamini, P.; Kemp, R. J.; Pringle, P. G. *J. Chem. Soc., Chem. Commun.* **1987**, 235–236. Martin, G. C.; Palenik, G. J.; Boncella, J. M. *Inorg. Chem.* **1990**, *29*, 2027–2030.

(3) $(\eta^5\text{-cp})RuCl(Cy_2PCH_2CH_3PCy_2)\cdot Et_2O$: ^1H NMR (C_6D_6) δ 4.71 s (C_5H_5); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 86.3 s. Anal. Calcd for $C_{35}H_{63}ClOP_2Ru$: C, 60.1; H, 9.08. Found: C, 60.1; H, 8.77.

(4) $[(\eta^5\text{-cp})Ru(NH_3)(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3\cdot Et_2O$: ^1H NMR (C_6D_6) δ 4.62 s (C_5H_5), 0.63 s (NH_3); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 86.7 s. Anal. Calcd for $C_{36}H_{66}F_3NO_4P_2RuS$: C, 52.2; H, 8.02; N, 1.68. Found: C, 52.3; H, M.54; N, 1.68.

(5) Crystal data for $[(\eta^5\text{-cp})Ru(NH_3)(PPh_3)_2]CF_3SO_3$: monoclinic $P2_1/n$, a = 12.,667 (1) Å, b = 14.356 (3) Å, c = 21.457 (4) Å, β = 96.58 (1)°, V = 3876 (2) Å^3, Z = 4, ρ(calcd = 1.448 g cm^{-3}, μ(Mo Kα) = 5.8 cm^{-1}, λ(Mo Kα) = 0.710 73 Å (graphite monochromator); 7990 unique reflections with $1° < 2\theta < 53°$ were collected, of which 4815 reflections with $I \geq 3\sigma(I)$ were used in refinement; R = 3.4%, R_w = 4.6%, GOF = 1.376.

(6) Gress, M. E.; Creutz, C.; Quicksall, C. D. *Inorg. Chem.* **1981**, *20*, 1522–1528.

(7) $(\eta^5\text{-cp})Ru(NH_2)(Cy_2PCH_2CH_2PCy_2)$: ^1H NMR (C_6D_6) δ 4.74 s (C_5H_5) 0 to −3 br (NH_2); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 92.5 s; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 77.4 s (C_5H_5), 41.4 m and 36.0 m (C–P's of Cy), 25–31 m (Cy's), 22.0 t (CH_2; $^1J(PC) + {}^3J(PC)$ = 19.7 Hz).

(8) An example of a complex having a substituted amide is $(\eta^5\text{-cp}^*)Ru(NPh_2)(PMe_3)_2$. See: Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tan, W.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 1444–1456.

(9) Park, S. Ph.D. Thesis, Tulane University, 1989.

formed in situ from Me_3N and $[Me_3O]BF_4$, to give the methylamine complex $[(\eta^5\text{-cp})Ru(NH_2Me)(Cy_2PCH_2CH_2PCy_2)]BF_4$ (eq 3). The formulation of this

$$(\eta^5\text{-cp})Ru(NH_2)(Cy_2PCH_2CH_2PCy_2) + Me_4N^+ \rightarrow [(\eta^5\text{-cp})Ru(NH_2Me)(Cy_2PCH_2CH_2PCy_2)]^+ + Me_3N \quad (3)$$

complex has been confirmed by its independent synthesis as the triflates salt from reacting a THF solution of $(\eta^5\text{-cp})RuCl(Cy_2PCH_2CH_2PCy_2)$ with silver triflate followed by methylamine.[10] An analogous synthetic procedure with *tert*-butylamine and $(\eta^5\text{-cp})RuCl(PPh_3)(P(OMe)_3)$ gives the primary amine complex $[(\eta^5\text{-cp})Ru(NH_2CMe_3)(PPh_3)(P(OMe)_3)]CF_3SO_3$, which has been characterized by X-ray crystallography.[11] An ORTEP representation of the cation is shown in Figure 2. The molecule has a "piano stool" structure with an Ru–N distance of 2.216 (2) Å, longer by 0.044 Å than is found in $[(\eta^5\text{-cp})Ru(NH_3)(PPh_3)_2]CF_3SO_3$. This elongation is due to the greater steric requirement of the *tert*-butylamine ligand.

The formation of $(\eta^5\text{-cp})Ru(NH_2)(Cy_2PCH_2CH_2PCy_2)$ demonstrates that monomeric unsubstituted amides of ruthenium(II) can be synthesized and that the complexed amide is more nucleophilic to a methyl cation than is Me_3N.[12]

Acknowledgment. We thank the Louisiana Educational Quality Support Fund, administered by the Louisiana Board of Regents, for support of this research. We thank Johnson Matthey Inc. for a loan of ruthenium trichloride.

Supplementary Material Available: Tables of positional parameters for non-H and H atoms, bond distances and angles, general displacement parameter expressions, root-mean-square amplitudes of anisotropic displacement, and torsion angles, along with crystallographic data and refinement details, for $[cpRu(NH_3)(PPh_3)_2]CF_3SO_3$ and $[cpRu(NH_2CMe_3)(PPh_3)(P(OMe)_3)]CF_3SO_3$ (45 pages); tables of observed and calculated structure factor amplitudes (111 pages). Ordering information is given on any current masthead page.

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[10] $[(\eta^5\text{-cp})Ru(NH_2Me)(Cy_2PCH_2CH_2PCy_2)]CF_3SO_3$: ^1H NMR (C_6D_6) δ 4.35 s (C_5H_5), 2.34 t (CH_3; $^3J(HH) = 5.8$ Hz), 2.7 br (NH_2); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 85.1 s. Anal. Calcd for $C_{33}H_{54}F_3NO_3P_2RuS$: C, 51.8; H, 7.12; N, 1.83. Found: C, 51.7; H, 7.22; N, 1.70.

[11] Crystal data for $[(\eta^5\text{-cp})Ru(NH_2CMe_3)(PPh_3)(P(OMe)_3)]CF_3SO_3$: monoclinic, $P2_1/c$, $a = 10.366$ (2) Å, $b = 21.862$ (2) Å, $c = 15.371$ (2) Å, $\beta = 92.33$ (1)°, $V. = 3481$ (2) Å^3, $Z = 4$, ρ(calcd) = 1.48 cm^{-3}, μ(Mo Kα) = 6.4 cm^{-1}, λ(Mo Kα) = 0.71073 Å (graphite monochromator); 6109 unique reflections with $1° < 2\theta < 50°$ were collected, of which 4778 reflections with $I \geq 3\sigma(I)$ were used in refinement; $R = 4.1\%$, $R_w = 6.3\%$, GOF = 2.249. The complex $(\eta^5\text{-cp})RuCl(PPh_3)(P(OMe)_3)$ has been prepared from $(\eta^5\text{-cp})RuCl(PPh_3)_2$ and $P(OMe)_3$. See: Joslin, F. L.; Mague, J. T.; Roundhill, D. M. *Organometallics*, in press.

[12] A similar alkyl group transfer has been observed for $(\eta^5\text{-cp})Re(NH_2)(NO)PPh_3$. See: Dewey, M. A.; Bakke, J. M.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1349–1351.

Distinct Chemical Reactivities of Tungsten Propargyl and Allenyl Complexes: Novel C–C Bond Formation of the Allenyl Ligand and Molecular Structure of a Tungsten Complex Containing an Azametallacyclobutane Ring

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Summary: The reactions of $Cp(CO)_3WCH{=}C{=}CH_2$ (**1**) with excess methylamine and with 1 equiv of ethanol produce the aza metallacycle complex $Cp(CO)_2WCH(CONHMe)CHMeNHMe$ (**3**) and $Cp(CO)_2W(\eta^3\text{-}CH(COOC_2H_5)CHCH_2)$ (**5**), respectively. The C–C bond formation takes place at the α-carbon of the original allenyl fragment. The reaction of $Cp(CO)_3WCH_2C{\equiv}CH$ (**2**) with amine yields $Cp(CO)_2W(\eta^3\text{-}CH_2C(CONHR)CH_2)$ (**4**), in which the amido group is attached at the β-carbon of the allyl group.

The chemistry of organometallic complexes containing one or more M–C σ-bonds has long been a subject of interest.[1] However, chemical reactivities of the transition-metal σ-allenyl complexes are less well-known,[2] due to their rarity. Recently, Wojcicki and co-workers[3] employed a substituted propargyl ligand as a template and reported the preparation of a polynuclear cluster containing a bridging allenyl ligand. We have observed the transformation of a simple propargyl ligand to an allenyl group in a mononuclear W complex.[4] We feel this body of work has revealed a new class of chemical reactions of transition-metal propargyl/allenyl complexes and hope to employ these complexes to further study their chemical re-

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[1] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 681.

[2] Several (π-allenyl)metal complexes are known: (a) Wojcicki, A. *Adv. Organomet. Chem.* **1974**, *12*, 31. (b) Lennon, P.; Madhavarao, M.; Rosan, A.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *108*, 93. (c) Benaim, J.; Merour, J. Y.; Roustan, J. L. *Tetrahedron Lett.* **1971**, 983. (d) Casey, C. P.; Austin, E. A. *J. Am. Chem. Soc.* **1988**, *110*, 7106 and references therein. (e) Jolly, P. W.; Pettit, R. *J. Organomet. Chem.* **1968**, *12*, 491. (f) Johnson, M. D.; Mayle, C. *J. Chem. Soc. D* **1969**, 192. (g) Roustan, J.; Cadiot, P. *C.R. Seances Acad. Sci., Ser. C* **1968**, *268*, 734. (h) Kroll, J. O.; Wojcicki, A. *J. Organomet. Chem.* **1974**, *66*, 95. (i) Jacobs, T. L. *The Chemistry of the Allenes*; Landor, S. R., Ed.; Academic Press: London, 1982; Volume 2, Chapter 4.3.

[3] Young, G. H.; Wojcicki, A.; Calligaris, M.; Nardin, G.; Bresciani-Pahor, N. *J. Am. Chem. Soc.* **1989**, *111*, 6890.

[4] Keng, R. S.; Lin, Y. C. *Organometallics* **1990**, *9*, 289.

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