Experimental Section

The reactions were carried out with the same batch of catalyst in the absence of oxygen and water under the following conditions: $(\equiv SiO)_2Ta{-}H$ (prepared by impregnation, 18.8×10^{-6} mol of Ta, 1 equiv), alkane (40 Torr, 43 equiv), and H_2 (630 Torr, 710 equiv) were heated with an oil bath to the desired temperature ($\pm 1\,^{\circ}C$) in a glass batch reactor (376 mL). During the reaction, aliquots were expended, brought to atmospheric pressure, and analyzed by gas chromatography (HP 5890 apparatus, Al_2O_3/KCl on fused silica column, 50m × 0.32mm). Alkanes and H_2 were dried over freshly regenerated molecular sieves (3Å) and deoxo traps before addition.

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[1] For the low-temperature hydrogenolysis of alkanes on group IV silica supported complexes, see: a) $(\equiv SiO)_3Zr{-}H$: C. Lecuyer, F. Quignard, A. Choplin, D. Olivier, J.-M. Basset, *Angew. Chem.* **1991**, *103*, 1692; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1660; J. Corker, F. Lefèbvre, C. Lécuyer, V. Dufaud, F. Quignard, A. Choplin, J. Evans, J.-M. Basset, *Science* **1996**, *271*, 966; b) $(\equiv SiO)_3Hf{-}H$: L. D'Ornelas, S. Reyes, F. Quignard, A. Choplin, J.-M. Basset, *Chem. Lett.* **1993**, 1931; c) $(\equiv SiO)_3Ti{-}H$: C. Rozier, G. P. Niccolaï, J.-M. Basset, *J. Am. Chem. Soc.* **1997**, *110*, 848.

[2] V. Dufaud, J.-M. Basset, *Angew. Chem.* **1998**, *110*, 848; *Angew. Chem. Int. Ed.* **1998**, *37*, 806; V. Dufaud, C. Marangelli, J.-M. Basset, unpublished results.

[3] For some examples of β-alkyl transfer, see: P. Watson, C. Roe, *J. Am. Chem. Soc.* **1982**, *104*, 6471; P. L. Watson, G. W. Parshall, *Acc. Chem. Res.* **1985**, *18*, 51; E. Bunel, B. Burger, J. Bercaw, *J. Am. Chem. Soc.* **1988**, *110*, 976; L. Schock, T. Marks, *J. Am. Chem. Soc.* **1990**, *110*, 7701; B. Burger, M. Thompson, D. Cotter, J. Bercaw, *J. Am. Chem. Soc.* **1990**, *112*, 1566; K. McNeill, R. A. Andersen, R. Bergman, *J. Am. Chem. Soc.* **1995**, *117*, 3625.

[4] For leading references on the insertion of an olefin in metal–alkyl bond, see: P. Cossee, *J. Catal.* **1964**, *3*, 80; H. Sinn, W. Kaminsky, *Adv. Organomet. Chem.* **1980**, *18*, 99; H. Sinn, W. Kaminsky, H.-J. Vollmer, R. Woldt, *Angew. Chem.* **1980**, *92*, 396; *Angew. Chem. Int. Ed. Engl.* **1980**, *19*, 390; R. F. Jordan, *Adv. Organomet. Chem.* **1991**, *32*, 325; T. J. Marks, *Acc. Chem. Res.* **1992**, *25*, 57.

[5] For the synthesis and characterization of $(\equiv SiO)_2Ta{-}H$, see: V. Vidal, A. Théolier, J. Thivolle-Cazat, J.-M. Basset, J. Corker, *J. Am. Chem. Soc.* **1996**, *118*, 4595.

[6] V. Vidal, A. Théolier, J. Thivolle-Cazat, J.-M. Basset, *Science* **1997**, *276*, 99; O. Maury, L. Lefort, V. Vidal, J. Thivolle-Cazat, J.-M. Basset, *Angew. Chem.* **1999**, *111*, 2121; *Angew. Chem. Int. Ed.* **1999**, *38*, 1952.

[7] F. Quignard, C. Lecuyer, A. Choplin, D. Olivier, J.-M. Basset, *J. Mol. Cat.* **1992**, *74*, 353.

[8] Nevertheless, since Ta–H is a d^2 surface complex, it is not possible to exclude processes that involve an increase in oxidation state, such as a direct oxidative addition of ethane or an α-alkyl transfer from the tantalum–ethyl fragment; the reverse step has been documented, see: P. R. Sharp, R. R. Schrock, *J. Organomet. Chem.* **1979**, *171*, 43; J. C. Hayes, G. D. N. Pearson, M. J. Cooper, *J. Am. Chem. Soc.* **1981**, *103*, 4648.

Unprecedented Formation of Five-, Six-, and Seven-Membered Metallacycles by Single and Double Insertion of Mono- and Disubstituted Alkynes into an Rh–O Bond[**]

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Metal alkynyl complexes are currently of great interest[1, 2] since they are valuable for constructing vinylidene or carbene complexes for use in organic synthesis.[3–8] Reactions of organotransition metal halides with 1-alkynes in the presence of anions such as PF_6^-, BF_4^-, and $CF_3SO_3^-$ are representative methods for the preparation of vinylidene complexes.[9] One *ortho*-methoxy group in (2,6-dimethoxyphenyl)diphenylphosphane (mdmpp) was demethylated in the reaction with the isoelectronic complexes $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = C_6Me_6, *p*-cymene, $C_6H_3Me_3$) and $[Cp^*MCl_2]_2$ (M = Rh, Ir) to give metal complexes with a (*P,O*)-chelating phosphane: $[(\eta^6\text{-arene})RuCl(\text{mdmpp-}\kappa P,\kappa O)]$[10, 11] and $[Cp^*MCl(\text{mdmpp-}\kappa P,\kappa O)]$[12, 13] ($Cp^* = C_5Me_5$). We recently reported the unprecedented insertion of tetracyanoethylene (tcne) and tetracyanoquinodimethane into the C–H bond adjacent to the M–O bonds of the above rhodium(III) and iridium(III) complexes to produce (*P,O*)-chelated $[Cp^*MCl[PPh_2\{2\text{-O-6-MeO-3-}(CH(CN)_2C(CN)_2)C_6H_2\}]$ in the case of tcne.[14]

Treatment of the ruthenium(III) complex with PhC≡CH in the presence of $NaPF_6$ in acetone/CH_2Cl_2 afforded the vinylidene complex $[(\eta^6\text{-arene})Ru(\text{mdmpp-}\kappa P,\kappa O)(=C=CHPh)]PF_6$.[15] However, treatment of $[Cp^*RhCl(\text{mdmpp-}\kappa P,\kappa O)]$ (**1**)[12] with 1-alkynes such as HC≡CCOOMe, PhC≡CH, and *n*BuC≡CH, and the disubstituted alkyne $C_2(CO_2Et)_2$ in the presence of $NaPF_6$ or KPF_6 resulted in unusual reactions (Scheme 1). In the reaction with HC≡CCOOMe, extraction of CO from the ester group of one and insertion of another 1-alkyne molecule into the Rh–O σ bond occurred to produce a seven-membered metallacycle, and reactions with HC≡CR led to the formation of complexes with five- and six-membered rings by double insertion of 1-alkynes into the Rh–O bond. The disubstituted alkyne also underwent single insertion into the Rh–O bond. Similar insertion of unsaturated molecules into the metal–oxygen bonds of metal alkoxides was achieved with cyclooctadiene[16] and perfluoroolefins[17] such as $F_2C{=}CF_2$ and hexafluorocyclobutene. The insertion of alkynes into the transition metal to oxygen σ bonds was achieved here for the first time.[18] Interestingly, these unprecedented reactions allow single and double insertion of alkynes into the Rh–O bond of **1** to be controlled by means of the alkyne substituents.

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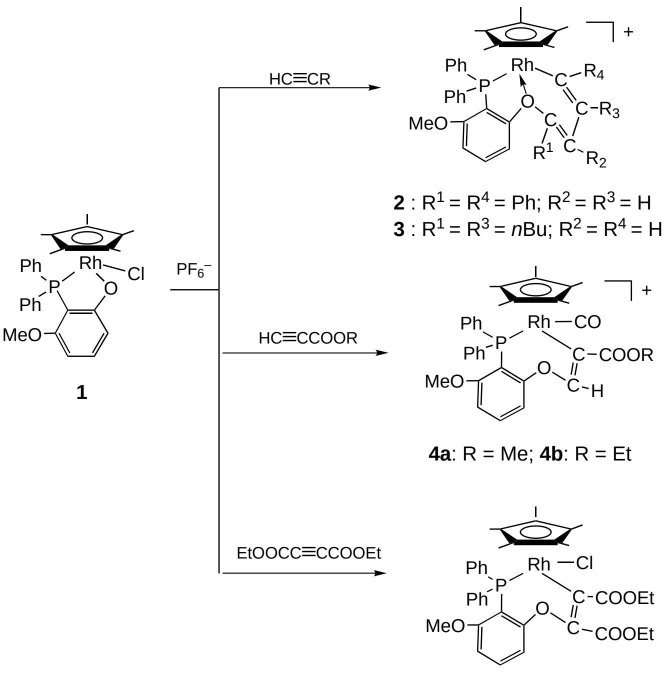


Scheme 1. Reactions of **1** with alkynes in the presence of PF_6^-.

Orange crystals, obtained from the reaction of **1** with an excess of ethynylbenzene were formulated as [Cp*Rh(mdmpp-*κP,κO*)(PhC≡CH)$_2$]PF_6 (**2a**-PF_6) on the basis of FAB mass spectrometric data. X-ray analysis showed the existence of two independent molecules, in which an Rh atom is surrounded by a novel tridentate ligand (P, O, C sites) derived from the head-to-head double-insertion of two PhC≡CH molecules into the Rh–O bond (Figure 1). A similar double insertion proceeded on treatment of **1** with 1-hexyne to give **3**, but X-ray analysis revealed that the structure resulted from a head-to-tail double insertion. The *n*Bu-substituted terminal C atom of the diene was connected to the O atom. The olefinic proton in the Rh–CH= moiety appeared as a doublet at $\delta = 5.69$ in the ^1H NMR spectrum due to coupling with ^{103}Rh. A similar insertion of two PhC≡CH molecules into an Ru–N bond was recently reported for the triruthenium cluster [Ru_3(μ-H)(μ-N=CPh_2)$(CO)_{10}$].[20]

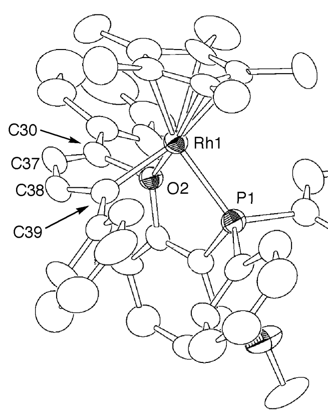
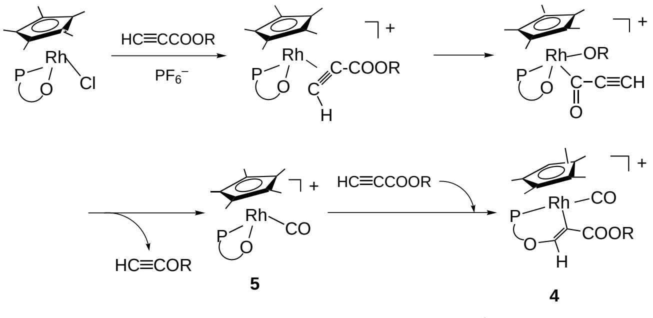


Figure 1. Perspective ORTEP view of the molecular structure of **2a** (showing one molecule; 50% probability thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Rh1-P1 2.312(2), Rh1-O2 2.239(5), Rh1-C39 2.108(9), O2-C30 1.447(10), C30-C37 1.34(1), C37-C38 1.43(1), C38-C39 1.36(1); P1-Rh1-O2 78.4(2), P1-Rh1-C39 92.2(3), O2-Rh1-C39 78.0(3).

Complex **1** reacted readily with an excess of HC≡CCOOMe under similar conditions to give yellow-orange crystals of **4a**-PF_6. The IR bands at 2060 and 1699 cm^{-1} were assigned to terminal CO and methoxycarbonyl groups, respectively. The presence of a PF_6^- ion was confirmed by a ν(PF) band at 837 cm^{-1}. The ^1H NMR spectrum showed three characteristic bands at $\delta = 1.54$ (d), 3.16 (s), and 3.76 (s), assigned to Cp*, methoxy, and methoxycarbonyl protons, respectively. X-ray analysis revealed the Rh atom to be surrounded by a CO and a bidentate P,C ligand formed by insertion of methyl propiolate into the metal–oxygen bond. The carbon atom bearing the methoxycarbonyl group occupied a rhodium site regioselectively due to the polarity of the Rh–O and C≡C bonds. A similar complex **4b** was obtained from the reaction of **1** with HC≡CCOOEt.

The formation of **4** in high yield in THF confirmed that the CO group originated from the propiolate. Abstraction of CO from ester groups is quite rare, although formation of [Ni(CO)$(PPh_3)_3$][21] from the reaction of [Ni$(cod)_2$] (cod = 1,5-cyclooctadiene) with triphenylphosphane and phenyl propionate and of [Rh(OAr)(CO)L_2][22] from MeCOOAr and [Rh(H)L_4] (L = phosphane ligand) have been documented.

Since compound **5**, prepared independently,[12] reacted readily with HC≡CCOOR to give **4**, we assume that formation of **4** involves initial oxidative addition of the ester and extraction of CO from an acyl group to give the carbonyl complex **5** (Scheme 2). The reaction is completed by CO abstraction, accompanied by elimination of HC≡COR. The formation of HC≡CCOEt and **4b** was confirmed by monitoring the reaction between **1** and HC≡CCOOEt by NMR spectroscopy.



Scheme 2. Possible pathway for the formation of **4** (P⌒O = PPh_2(2-O-6-$MeOC_6H_3$)).

Reactions with internal alkynes such as MeC≡CPh and EtOOCC≡CCOOEt were carried out in the presence of KPF_6. The former failed to react, whereas the latter produced reddish orange **6** (Scheme 1). The IR spectrum showed bands at 1705 and 1589 cm^{-1} for a carbonyl group and a C–C double bond. However, there was no band at about 840 cm^{-1} for a PF_6

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group. In the $^{31}P\{^1H\}$ NMR spectrum, no signal due to a PF_6 moiety was observed, and only a doublet at $\delta = 10.28$ ($J_{Rh,P} = 136.8$ Hz) appeared. In the ^1H NMR spectrum, methyl signals of the ester groups appeared at $\delta = 1.03$ and 1.27 as a triplet, and the methylene protons gave rise to two multiplets at $\delta = 4.03$ and 4.18 due to the nonequivalence of the methylene protons that results from the asymmetric coordination environment of the Rh atom. The spectroscopic data suggested that the complex was a seven-membered metallacycle derived from the insertion of EtOOCC≡CCOOEt. The proposed structure was confirmed by X-ray analysis (Figure 2). When this reaction was performed without PF_6^- ions, the starting materials were recovered quantitatively. The presence of PF_6^- was indispensable for this reaction.

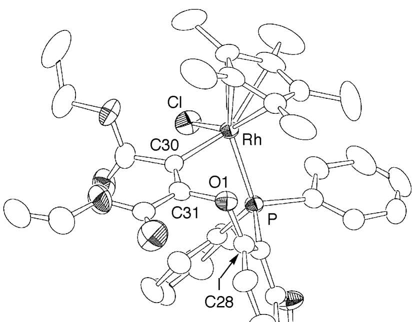

Figure 2. Perspective ORTEP view of the molecular structure of **6** (50% probability thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Rh1-Cl1 2.399(1), Rh1-P1 2.302(1), Rh1-C30 2.044(6), C30-C31 1.324(8), C31-O1 1.415(7), O1-C28 1.394(6); P1-Rh1-Cl1 89.90(5), P1-Rh1-C30 85.3(1), O1-Rh1-C30 93.7(2).

Further mechanistic studies and reactions with other small molecules are now in progress.

Experimental Section

2a-PF_6: An excess of $NaPF_6$ was added to a solution of **1** (50 mg, 0.086 mmol) and PhC≡CH (0.1 mL) in CH_2Cl_2 (15 mL) and acetone (10 mL) at room temperature. After 4 h, the solvent was removed, and the residue was extracted with CH_2Cl_2. The CH_2Cl_2 was removed to give an oily residue, which was purified by chromatography on silica gel with CH_2Cl_2/*n*-hexane (1/5) as eluent. The reddish brown eluate was dried, and the residue was recrystallized from CH_2Cl_2/diethyl ether to give orange crystals of **2a**-PF_6 (27 mg, 35%). IR (Nujol): $\tilde{\nu} = 1591$, 1568, 837 cm^{-1}; UV (CH_2Cl_2): $\lambda_{max} \approx 360$, 286 nm; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.35$ (d, J(P,H) = 2.5 Hz, Cp*, 15H), 3.30 (s, OMe, 3H), 6.3–7.6 (m, CH= and ArH, 25H); ^{31}P NMR (100 MHz, $CDCl_3$): $\delta = 36.9$ (d, J(Rh,P) = 157.5 Hz), −143.8 (sept, J(P,F) = 717 Hz); FAB MS (*m*/*z* of cationic part): 749 (749.7); C,H analysis calcd for $C_{45}H_{43}O_2P_2F_6Rh$: C 60.41, H 4.84; found: C 60.12, H 4.83. Crystal data: space group $P2_1/a$ (No. 14) with $a = 20.003(4)$, $b = 15.555(5)$, $c = 26.289(4)$ Å, $\beta = 90.24(2)°$, $V = 8179(3)$ Å^3 at 26 °C, $Z = 8$ (two independent molecules per unit cell). The structure was solved by Patterson methods and refined by full-matrix least-squares techniques for 14832 reflections having $I > -10.0\sigma(I)$ to $R = 0.133$, $Rw = 0.181$, $R1 = 0.066$ (for 7979 reflections); GOF 1.60.

3-PF_6: A solution of **1** (50 mg, 0.086 mmol), 1-hexyne (0.1 mL) and an excess of $NaPF_6$ in CH_2Cl_2/acetone (15/10 mL) was stirred for 4 h. The solvent was removed, and the residue extracted with CH_2Cl_2. After the solution was concentrated to 3 mL, diethyl ether was added to give orange crystals of **3**-PF_6 (24 mg, 32%). IR (Nujol): $\tilde{\nu} = 1660$, 1593, 837 cm^{-1}; UV (CH_2Cl_2): $\lambda_{max} \approx 390$ (sh), 283 nm; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.68$ (t, J(H,H) = 6.8 Hz, CH_3, 3H), 1.03 (t, J(H,H) = 6.8 Hz, CH_3, 3H), 1.39 (d, J(P,H) = 2.5 Hz, Cp*, 15H), 1.2–2.8 (m, $(CH_2)_3$, 12H), 3.38 (s, OMe, 3H), 5.56 (s, CH=, 1H), 5.69 (d, J(Rh,H) = 15.0 Hz, 1H), 6.6–7.8 (m, ArH, 13H); ^{31}P NMR (100 MHz, $CDCl_3$): $\delta = 44.8$ (d, J(Rh,P) = 157.5 Hz), −143.8 (J(P,F) = 712 Hz); FAB MS (*m*/*z* of cation part): found: 709; calcd 707.7; C,H analysis calcd for $C_{41}H_{51}O_2P_2F_6Rh$: C 57.62, H 6.01; ound C 57.65, H 5.85. Crystal data: space group $P\bar{1}$ (No. 2), $a = 11.575(4)$, $b = 16.67(1)$, $c = 10.800(5)$ Å, $\alpha = 90.17(5)°$, $\beta = 99.46(3)°$, $\gamma = 93.41(4)°$, $V = 2051(1)$ Å^3 at 26 °C, $Z = 2$. The structure was solved by Patterson methods and refined by full-matrix least-squares techniques for all unique reflections (5376) to $R = 0.231$, $Rw = 0.092$ and $R1 = 0.073$ (for 2310 reflections); GOF 1.25.

4a-PF_6: Yellow-orange crystals of **4a**-PF_6 (61 mg, 40%) were obtained from **1** (110 mg, 0.189 mmol), HC≡CCOOMe (0.1 mL), and an excess of $NaPF_6$ by a procedure similar to that for **3**-PF_6. IR (Nujol): $\tilde{\nu}$2060, 1699, 1583, 837 cm^{-1}; UV (CH_2Cl_2): $\lambda_{max} = 293$ nm; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.54$ (d, J(P,H) = 2.5 Hz, Cp*, 15H), 3.16 (s, OMe, 3H), 3.76 (s, OMe, 3H), 6.7–7.8 (m, ArH, 13H), 7.96 (s, CH=, 1H); ^{31}P NMR (100 MHz, $CDCl_3$): $\delta = 3.12$ (d, J(Rh,P) = 122.3 Hz, 1P), −143.9 (sept, J(P,F) = 712 Hz, PF_6); C,H analysis calcd for $C_{34}H_{35}O_5P_2F_6Rh$: C 51.14, H 4.31; found C 50.89, H 4.40. Crystal data: space group $P2_1/a$ (No. 14), $a = 15.410(5)$, $b = 22.199(4)$, $c = 10.602(4)$ Å, $\beta = 110.11(3)°$, $V = 3405(1)$ Å^3 at −100 °C, $Z = 4$ (at 26 °C: $b = 14.582(3)$, $c = 14.426(3)$ Å, $V = 3463(1)$ Å^3, $Z = 4$). The structure was solved by direct methods (SIR92) and refined by full-matrix least-squares techniques for 5097 reflections having $I > 2.5\sigma(I)$ to $R = 0.071$, $Rw = 0.132$, $R1 = 0.049$ (for 5097 reflections); GOF 1.83.

4b-PF_6: Orange (32%): IR (Nujol): $\tilde{\nu} = 2060$, 1695, 1585, 1564, 837 cm^{-1}; UV (CH_2Cl_2): $\lambda_{max} = 310$ nm; ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.28$ (t, J(H,H) = 7.5 Hz, Me, 3H), 1.54 (d, J(P,H) = 2.5 Hz, Cp*, 15H), 3.16 (s, OMe, 3H), 4.22 (q, J(H,H) = 7.5 Hz, OCH_2, 2H), 6.7–7.8 (m, ArH, 13H), 7.96 (s, CH=, 1H); ^{31}P NMR (100 MHz, $CDCl_3$): $\delta = 3.15$ (d, J(Rh,P) = 124.9 Hz, 1H), −143.9 (J(P,F) = 711.0 Hz, PF_6); C,H analysis calcd for $C_{35}H_{37}O_5P_2F_6Rh$: C 51.80, H 4.51; found: C 51.48, H 4.57.

6: Orange crystals (45 mg, 63%) were obtained from **1** (55 mg, 0.095 mmol), EtOOCC≡CCOOEt (0.1 mL), and an excess of $NaPF_6$. IR (Nujol): $\tilde{\nu} = 1705$ (C=O), 1589 cm^{-1} (C=C); ^1H NMR (250 MHz, $CDCl_3$): $\delta = 1.03$ (t, J(H,H) = 7.2 Hz, Me, 3H), 1.27 (t, J(H,H) = 7.2 Hz, Me, 3H), 1.26 (d, J(P,H) = 3.2 Hz, Cp*, 15H), 3.03 (s, OMe, 3H), 4.03 (m, CH_2, 2H), 4.18 (m, CH_2, 2H), 7.0–7.9 (m, Ph, 13H); ^{31}P NMR (100 MHz, $CDCl_3$): $\delta = 10.28$ (d, J(Rh,P) = 136.8 Hz, 1P); C,H analysis calcd for $C_{37}H_{41}O_6PClRh \cdot 0.5\,CH_2Cl_2$: C 56.76, H 5.34; found: C 56.56, H 5.22. Crystal data for **6** · $0.5\,CH_2Cl_2$: space group $Pna2_1$ (No. 33), $a = 16.466(3)$, $b = 14.582(3)$, $c = 14.426(3)$ Å, $V = 3463(1)$ Å^3 at 25 °C, $Z = 4$. The structure was solved by direct methods (SIR92) and refined by full-matrix least-squares techniques for 3179 reflections having $I > 2.0\sigma(I)$ to $R = 0.039$, $Rw = 0.035$, $R1 = 0.029$ (for 2771 reflections); GOF 1.37.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-132821 (**4a**), -132822 (**3**), -132823 (**6**) and -132824 (**2a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[1] L. T. Scott, M. J. Cooney, D. Johnels, *J. Am. Chem. Soc.* **1990**, *112*, 4054.

[2] M. H. Chisholm, *Angew. Chem.* **1991**, *103*, 690; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 673.

[3] B. M. Trost, G. Dyker, R. J. Kulawiec, *J. Am. Chem. Soc.* **1990**, *112*, 7809.

[4] L. S. Liebeskind, R. Chidambaram, D. Mitchell, B. S. Foster, *Pure Appl. Chem.* **1988**, *60*, 27.

[5] A. G. M. Barrett, J. Mortier, M. Sabat, M. A. Sturgess, *Organometallics* **1988**, *7*, 2553.

[6] R. Mahe, P. H. Dixneuf, S. Lecolier, *Tetrahedron Lett.* **1986**, *27*, 6333.

[7] A. G. M. Barrett, N. E. Carpenter, *Organometallics* **1987**, *6*, 2249.

[8] S. L. Buchwald, R. H. Grubbs, *J. Am. Chem. Soc.* **1983**, *105*, 5490.

[9] M. I. Bruce, *Chem. Rev.* **1991**, *91*, 197, and references therein.

[10] Y. Yamamoto, R. Sato, F. Matsuo, C. Sudoh, T. Igoshi, *Inorg. Chem.* **1996**, *35*, 2329.

[11] Y. Yamamoto, R. Sato, M. Ohshima, F. Matsuo, C. Sudoh, *J. Organomet. Chem.* **1995**, *489*, C68.

[12] X.-H. Han, Y. Yamamoto, *J. Organomet. Chem*. **1998**, *561*, 157.

[13] Y. Yamamoto, K. Kawasaki, S. Nishimura, *J. Organomet. Chem.* **1999**, *587*, 49.

[14] Y. Yamamoto, X.-H. Han, K. Sugawara, S. Nishimura, *Angew. Chem.* **1999**, *112*, 1318; *Angew. Chem. Int. Ed.* **1999**, *38*, 1242.

[15] Y. Yamamoto, T. Tanase, C. Sudoh, T. Turuta, *J. Organomet. Chem.* **1998**, *569*, 29.

[16] B. de Bruin, M. J. Boerakker, J. A. Brands, J. J. J. M. Donners, M. P. J. Donners, R. de Gelder, J. M. M. Smits, A. W. Gal, A. L. Spek, *Chem. Eur. J.* **1999**, *5*, 2921.

[17] M. H. Chisholm, F. A. Cotton, M. W. Extine, W. W. Reichert, *J. Am. Chem. Soc.* **1978**, *100*, 1727.

[18] The insertion of alkynes into the Pt–OH bond is cited as H. Jin, PhD Thesis, The Australian National University, **1990** in ref. [19], but details were not reported.

[19] M. A. Bennett, H. Jin, S. Li, L. M. Rendina, A. C. Willis, *J. Am. Chem. Soc.* **1995**, *117*, 8335.

[20] J. A. Cabeza, I. Rio, R. J. Franco, F. Grepioni, V. Riera, *Organometallics* **1997**, *16*, 2763.

[21] T. Yamamoto, J. Ishizu, T. Kohara, S. Komiya, A. Yamamoto, *J. Am. Chem. Soc.* **1980**, *102*, 3758.

[22] T. Yamamoto, S. Miyashita, Y. Naito, S. Komiya, T. Ito, A. Yamamoto, *Organmetallics* **1982**, *1*, 808.

A Grid Complex $[Cu^{I}_{4}L_{2}]^{4+}$ and a Mixed-Valent Complex $[Cu^{II}Cu^{I}L(MeCN)_{2}]^{3+}$ of the Pyridazine-Containing Macrocycle L**

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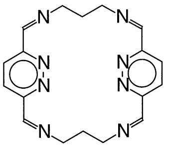

L

The Schiff base macrocycle L, obtained from the [2+2] condensation of 3,6-diformylpyridazine[1–4] and 1,3-diaminopropane, has allowed the isolation of a wide range of transition metal complexes with intriguing properties, in particular redox[1, 5, 6] and magnetic properties.[5–7] To date, many pyridazine-bridged or phthalazine-bridged dicopper(II) complexes,[8–10] but few copper(I) complexes[11–15] and, to our knowledge, no mixed-valent copper complexes, have been isolated. The structure, magnetochemistry, and electrochemistry of the first example of a macrocyclic pyridazine-bridged dicopper complex was reported recently.[5] In contrast to other pyridazine-bridged dicopper complexes, two well-separated one-electron reductions were observed for this dicopper(II) complex, as is seen for related phenolate-bridged complexes,[16] except that, as expected, they occur at more positive potentials due to the π-acceptor properties of L. We report here on the formation and characterization of the mixed-valent complex **1** and the air-stable tetracopper(I) grid complex $[Cu^{I}_{4}L_{2}](PF_{6})_{4}$ (**2**) of the Schiff-base macrocyclic ligand L.

$[Cu^{II}Cu^{I}L(MeCN)_{2}](ClO_{4})_{2}(PF_{6})$ **1**

The mixed-valent $Cu^{II}Cu^{I}$ complex **1** is formed by a transmetallation reaction in acetonitrile (see the Experimental Section) and crystallized, in air, in 41 % yield, by diffusion of diethyl ether into the reaction solution. The IR spectrum of **1** shows that the macrocycle is intact. The structure determination of **1**·MeCN (Figure 1) reveals a similar overall structure to that of the dicopper(II) analogue $[Cu^{II}_{2}L(MeCN)_{2}]^{4+}$ (**3**).[5] The copper centers are doubly bridged by the pyridazine groups and the macrocycle is fairly flat (the pyridazine ring planes intersect at 23.5(2)°; cf. 29.67(7)° for **3**). In each case four of the nitrogen donors come from the macrocycle (N_{macro}) and the fifth from an acetonitrile solvent molecule. However, the copper ions have distinct geometries consistent with the mixed-valent complex being class I

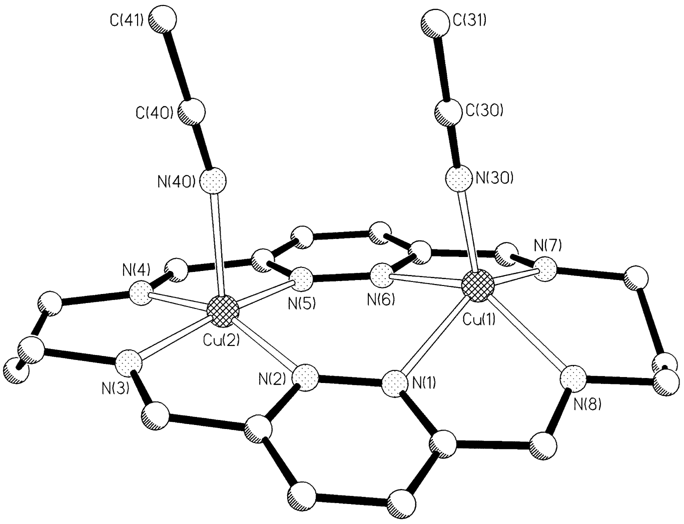

Figure 1. Perspective view of the cation of **1**, $[Cu^{II}Cu^{I}L(MeCN)_{2}]^{3+}$. Selected interatomic distances [Å] and angles [°]: Cu(1)-N(30) 1.931(4), Cu(1)-N(7) 2.038(4), Cu(1)-N(8) 2.105(4), Cu(1)-N(1) 2.151(3), Cu(1)-N(6) 2.289(3), Cu(2)-N(3) 1.978(3), Cu(2)-N(5) 2.008(3), Cu(2)-N(4) 2.034(3), Cu(2)-N(2) 2.072(3), Cu(2)-N(40) 2.157(4), Cu(1)···Cu(2) 3.9599(9); N(30)-Cu(1)-N(7) 115.87(15), N(30)-Cu(1)-N(8) 115.62(14), N(7)-Cu(1)-N(8) 91.49(15), N(30)-Cu(1)-N(1) 102.05(14), N(7)-Cu(1)-N(1) 141.48(13), N(8)-Cu(1)-N(1) 77.37(13), N(30)-Cu(1)-N(6) 104.39(13), N(7)-Cu(1)-N(6) 75.18(14), N(8)-Cu(1)-N(6) 139.62(13), N(1)-Cu(1)-N(6) 89.64(12), N(3)-Cu(2)-N(5) 168.97(13), N(3)-Cu(2)-N(4) 92.85(14), N(5)-Cu(2)-N(4) 80.48(13), N(3)-Cu(2)-N(2) 80.42(13), N(5)-Cu(2)-N(2) 102.93(13), N(4)-Cu(2)-N(2) 160.04(13), N(3)-Cu(2)-N(40) 92.51(14), N(5)-Cu(2)-N(40) 97.09(14), N(4)-Cu(2)-N(40) 98.03(15), N(2)-Cu(2)-N(40) 101.00(14), C(30)-N(30)-Cu(1) 178.2(4), C(40)-N(40)-Cu(2) 168.1(4).

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