COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Terminal ruthenium carbido complexes as σ-donor ligands†

Andrew Hejl, Tina M. Trnka, Michael W. Day and Robert H. Grubbs*
Arnold and Mabel Beckman Laboratory of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA. E-mail: rhg@its.caltech.edu

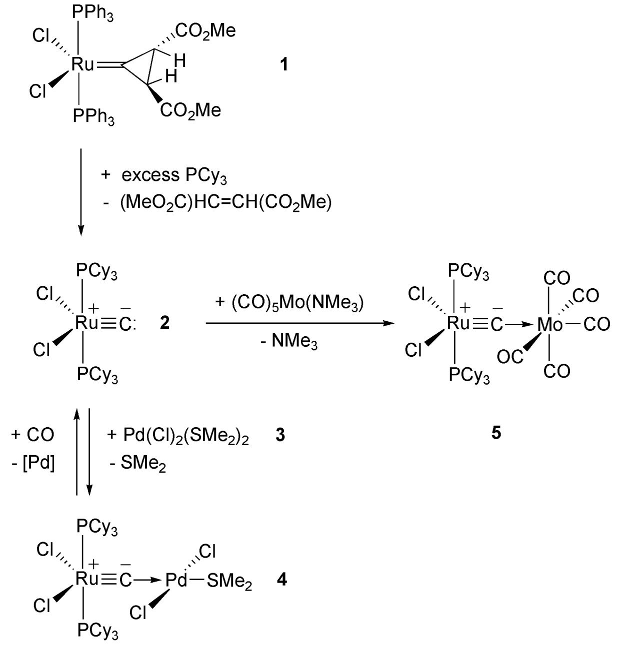
Received (in Purdue, IN, USA) 13th August 2002, Accepted 6th September 2002
First published as an Advance Article on the web 30th September 2002

The terminal carbido ligand of $(PCy_3)_2(Cl)_2RuC$ coordinates to other metal centers in a σ-donor fashion, as in $(PCy_3)_2(Cl)_2Ru{\equiv}C{-}Pd(Cl)_2(SMe_2)$ and $(PCy_3)_2(Cl)_2Ru{\equiv}C{-}Mo(CO)_5$.

In 1995, we reported that the bis(triphenylphosphine)ruthenium benzylidene complex $(PPh_3)_2(Cl)_2Ru{=}CHPh$ reacts with *trans*-2,3-dicarbomethoxymethylenecyclopropane to yield a unique 2,3-dicarbomethoxycyclopropane carbene complex, $(PPh_3)_2(Cl)_2Ru{=}C(CHCO_2Me)_2$ (**1**).[1] Recent work by Heppert and co-workers, in which they obtain the terminal carbido complex $(PCy_3)_2(Cl)_2RuC$ (**2**) from the closely related bis(tricyclohexylphosphine) derivative $(PCy_3)_2(Cl)_2Ru{=}CHPh$ plus *trans*-2,3-dicarbomethoxymethylenecyclopropane,[2] prompted us to re-examine the chemistry of **1**.

The addition of at least two equivalents of PCy_3 to **1** causes the instant release of dimethyl fumarate and provides **2** in good yield (70%) (Scheme 1).‡ This reaction confirms that the more electron-donating PCy_3 ligands are required for olefin elimination, and provides an isolated product yield greater than for the transformation of $(PCy_3)_2(Cl)_2Ru{=}CHPh$ to **2** (54%).[2] Thus, **2** is accessible by at least two straightforward routes. In contrast to anionic carbido complexes of molybdenum and tungsten,[3] **2** also has excellent stability toward air and moisture. For these reasons, it is a promising candidate for potential synthetic applications.

For example, complex **2** displaces one of the dimethylsulfide ligands in $Pd(Cl)_2(SMe)_2$ (**3**)[4] to form the bimetallic μ-carbido product $(PCy_3)_2(Cl)_2Ru{\equiv}C{-}Pd(Cl)_2(SMe_2)$ (**4**) (Scheme 1).[5] We initially chose **3** as a coordination partner based on its compact square-planar geometry, but the analogous reaction with octahedral $(CO)_5Mo(NMe_3)$[6] is also successful and provides $(PCy_3)_2(Cl)_2Ru{\equiv}C{-}Mo(CO)_5$ (**5**) (Scheme 1). Unfortunately, **5** cannot be isolated because it is unstable in solution, presumably the result of unfavorable steric interactions between the PCy_3 ligands and the equatorial tetracarbonyl 'wall'.



Scheme 1

The coordination of an isolated terminal carbido complex to another metal center establishes that the carbido ligand can function in a σ-donor capacity. In this sense, **2** is related to terminal oxo and nitrido complexes that form Lewis acid adducts, such as $(Bu^tCH_2)_3(Br)W{=}O{-}AlBr_3$ and $(PMe_2Ph)_2Cl_2Re{\equiv}N{-}BCl_3$.[7] This behavior also is consistent with the donor–acceptor bonding model described by Frenking and co-workers for the metal–carbido interaction, which predicts a nucleophilic ligand with a lone pair available for bonding.[8]

Both **4** and **5** are characterized by distinctive ^{13}C NMR resonances for the μ-carbido ligands at δ 381.2 and 446.3, respectively. The further downfield shift of **5** likely reflects the weaker carbido–molybdenum interaction in this molecule. In comparison, the ^{13}C resonance of the terminal carbido ligand in **2** appears at δ 471.8.[2] The resonances for other known μ-carbido complexes vary widely from δ 211–406.[9]

The crystal structures of **2**, **3**, and **4** are shown in Fig. 1.§ The ruthenium–carbon distance in **2** [1.632(6) Å] is slightly shorter than that in the *N*-heterocyclic carbene derivative $(H_2IMes)(PCy_3)(Cl)_2RuC$ (H_2IMes = 1,3-dimesitylimidazolidine-2-ylidene) [1.650(2) Å].[2] The ruthenium–carbon distance in **4** [1.662(2) Å] is slightly longer than in **2** (Table 1), but it is comparable to the distance in Werner's cationic ruthenium carbyne complex $[(PPr^i_3)_2(Cl)(CF_3CO_2)Ru{\equiv}CCH_2Ph][BAr_4]$ [1.660(4) Å].[10] The palladium–carbon distance in **4** [1.946(2) Å] is similar to that in $[(Et_2H_2Im)PdCl(\mu\text{-}Cl)]_2$ [1.946(3) Å] (Et_2H_2Im = 1,3-diethylimidazolidine-2-ylidene),[11] in which the *N*-heterocyclic carbene acts as a σ-donor ligand. On this basis, we assign the ruthenium–carbon interaction in **4** as a triple bond and the palladium–carbon interaction as a single bond. A similar formulation has been made for $(Tp')(CO)_2Mo{\equiv}C{-}Fe(CO)_2(Cp)$ and $(Me_3CO)_3W{\equiv}C{-}Ru(CO)_2(Cp)$, although the allylidene alternative [M=C=M] is also possible, as in the case of $(TPP)Fe{=}C{=}Re(CO)_4Re(CO)_5$.[9]

Further comparison of **4** with its components reveals that the [Pd–S] distance in **4** is slightly longer (by 0.037 Å) than in **3** (Table 1). This difference indicates that $(PCy_3)_2(Cl)_2RuC$ has a somewhat stronger structural *trans* influence than SMe_2. However, the carbido–palladium interaction is still relatively weak and easily disrupted. For example, the reaction of **4** with carbon monoxide regenerates **2** and provides uncharacterized palladium byproducts (Scheme 1). The attempted coordination of **3** to $(H_2IMes)(PCy_3)(Cl)_2RuC$ also fails, presumably because the potential strength of the carbido–palladium interaction is not great enough to overcome the steric bulk of the H_2IMes ligand.

Previous work has shown that the $[(PR_3)_2(Cl)_2Ru]$ scaffold can be used to isolate ruthenium carbene complexes with a wide variety of substituents,[1,12] and the discovery that this same

---

† Electronic supplementary information (ESI) available: additional crystallographic information. See http://www.rsc.org/suppdata/cc/b2/b207903h/

DOI: 10.1039/b207903h

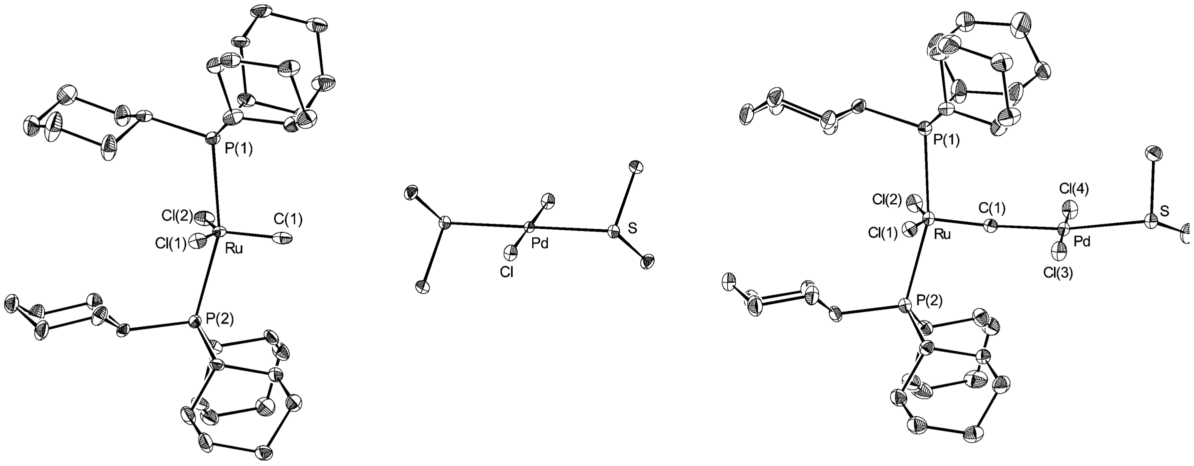


Fig. 1 Crystal structures of $(PCy_3)_2(Cl)_2RuC$ (**2**), $Pd(Cl)_2(SMe_2)_2$ (**3**), and $(PCy_3)_2(Cl)_2Ru{\equiv}C–Pd(Cl)_2(SMe_2)$ (**4**). For clarity, all hydrogen atoms have been omitted. Displacement ellipsoids are drawn at 50% probability.

Table 1 Selected bond lengths (Å) and angles (deg)

	Complex **2**	Complex **3**	Complex **4**
[Ru–C(1)]	1.632(6)	—	1.662(2)
[Ru–Cl][a]	2.376(2)	—	2.350(1)
[Ru–P][a]	2.427(2)	—	2.436(1)
[P–C][a]	1.854(6)	—	1.853(2)
[Pd–Cl][a]	—	2.292(1)	2.301(1)
[Pd–S]	—	2.319(1)	2.356(1)
[Pd–C]	—	—	1.946(2)
[Cl–Ru–Cl]	156.66(5)	—	158.27(2)
[P–Ru–P]	160.66(5)	—	162.89(2)
[Cl–Pd–Cl]	—	180	178.13(2)
[Ru–C–Pd]	—	—	175.1(1)
[L–Pd–S]	—	180	170.50(5)

[a] Average values.

scaffold can support terminal and bridging carbido ligands is an exciting development. In this communication, we have demonstrated that the terminal carbido complex **2** can coordinate to other metal centers in a σ-fashion, which contributes to our understanding of these unusual ligands.

This research was supported by the US National Science Foundation. We thank Lawrence M. Henling for contributions to the crystallography, Jeremy May for chemicals, and Prof. Jonas Peters and Andrew Waltman for helpful discussions.

Notes and references

‡ *Synthesis of* **2**: Under a nitrogen atmosphere, 40.0 mg (0.143 mmol) of PCy_3 was added to a solution of 30.1 mg (0.0353 mmol) of **1** in 3 mL CH_2Cl_2. This solution was stirred for 4 h at r.t., and then the solvent was removed under vacuum. The resulting solid was washed with hexanes and dried to yield 18.5 mg of **2** as a light brown powder (70%). *Synthesis and characterization of* **4**: Under a nitrogen atmosphere, 50.2 mg (0.0674 mmol) of **2** and 20.4 mg (0.0676 mmol) of **3** were dissolved in 5 mL CH_2Cl_2. After stirring for 5 h at r.t., the solvent was removed under vacuum. The resulting solid was reprecipitated from benzene/hexanes and washed with hexanes to yield 42.1 mg of **4** as a pale yellow powder (63%). ^1H NMR (299.82 MHz, $CDCl_3$, δ): 2.74 (m, Cy), 2.32 (pseudodoublet, Cy), 2.26 (s, SMe), 1.87 (broad s, Cy), 1.70 (pseudotriplet, Cy), 1.30 (m, Cy). $^{31}P\{^1H\}$ NMR (121.64 MHz, $CDCl_3$, δ): 40.85 (s). $^{13}C\{^1H\}$ NMR (125.72 MHz, $CDCl_3$, δ): 381.23 (m, μ-C), 128.30 (s, SCH_3), 32.96 (t, J_{CP} = 10 Hz, Cy), 30.59 (s, Cy), 28.27 (t, J_{CP} = 5 Hz, Cy), 26.84 (s, Cy). *Generation and characterization of* **5**: A screw-cap NMR tube was charged with 50.6 mg (0.0679 mmol) of **2**, 20.1 mg (0.0681 mmol) of $[(CO)_5Mo(NMe_3)]$, and 0.7 mL of CD_2Cl_2. Spectra were recorded after 6 h at r.t. ^1H NMR (299.82 MHz, CD_2Cl_2, δ): 2.58 (s, Cy), 2.01 (s, Cy), 1.68 (m, Cy), 1.46 (m, Cy), 1.13 (m, Cy). $^{31}P\{^1H\}$ NMR (121.64 MHz, CD_2Cl_2, δ): 33.80 (s). $^{13}C\{^1H\}$ NMR (125.72 MHz, CD_2Cl_2, δ): 446.31 (s, RuC), 209.12 (s, CO), 205.15 (s, CO), 32.98 (t, J_{CP} = 9 Hz, Cy), 30.87 (s, Cy), 28.26 (t, J_{CP} = 6 Hz, Cy), 27.00 (s, Cy). IR (ν_{CO}, cm^{-1}, CH_2Cl_2): 2073 (m), 1966 (s), 1943 (s).

§ *Crystal data* for **2**: $C_{37}H_{66}Cl_2P_2Ru{\cdot}C_6H_6$, M = 822.92, monoclinic, space group $P2_1/n$ (#14), a = 9.9665(7), b = 19.737(2), c = 21.505(2) Å, β = 92.128(1)°, V = 4227.3(5) Å^3, T = 98 K, Z = 4, μ(Mo-Kα) = 0.601 mm^{-1}, 62446 measured reflections, 10049 unique, 7579 reflections with $I > 2\sigma(I)$, all unique used in refinement, final R_1 = 0.1132, wR_2 = 0.1505. *Crystal data* for **3**: $C_4H_{12}Cl_2PdS_2$, M = 301.56, monoclinic, space group $P2_1/n$ (#14), a = 8.357(1), b = 5.9396(7), c = 10.065(2) Å, β = 106.321(2)°, V = 479.5(1) Å^3, T = 98 K, Z = 2, μ(Mo-Kα) = 2.851 mm^{-1}, 8998 measured reflections, 1125 unique, 1057 reflections with $I > 2\sigma(I)$, all unique used in refinement, final R_1 = 0.0191, wR_2 = 0.0390. *Crystal data* for **4**: $C_{39}H_{72}Cl_4P_2PdRuS{\cdot}2C_6H_6$, M = 1140.45, triclinic, space group $P1$ (#2), a = 9.9306(4), b = 12.5669(5), c = 22.8075(9) Å, α = 87.842(1), β = 89.414(1), γ = 67.978(1)°, V = 2636.7(2) Å^3, T = 98 K, Z = 2, μ(Mo-Kα) = 0.964 mm^{-1}, 54747 measured reflections, 12240 unique, 10533 reflections with $I > 2\sigma(I)$, all unique used in refinement, final R_1 = 0.0324, wR_2 = 0.0523. CCDC 190234, 189804 and 186479. See http://www.rsc.org/suppdata/cc/b2/b207903h/ for crystallographic data in CIF or other electronic format.

1 Z. Wu, S. T. Nguyen, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1995, **117**, 5503–5511.
2 R. G. Carlson, M. A. Gile, J. A. Heppert, M. H. Mason, D. R. Powell, D. V. Velde and J. M. Vilain, *J. Am. Chem. Soc.*, 2002, **124**, 1580–1581.
3 (*a*) J. C. Peters, A. L. Odom and C. C. Cummins, *Chem. Commun.*, 1997, 1995–1996; (*b*) A. E. Enriquez, P. S. White and J. L. Templeton, *J. Am. Chem. Soc.*, 2001, **123**, 4992–5002; (*c*) J. B. Greco, J. C. Peters, T. A. Baker, W. M. Davis, C. C. Cummins and G. Wu, *J. Am. Chem. Soc.*, 2001, **123**, 5003–5013.
4 P. K. Byers, A. J. Canty, H. Jin, D. Kruis, B. A. Markies, J. Boersma and G. van Koten, *Inorg. Synth.*, 1998, **32**, 162–164.
5 Heppert and co-workers have reported the related complex $[(PCy_3)_2(Cl)_2Ru(\mu\text{-}CCuCl)]_2$ at a meeting. M. H. Mason, R. G. Carlson, M. A. Gile, J. Heppert, D. Powell and J. M. Vilain, *ACS National Meeting Book of Abstracts*, American Chemical Society, Orlando, FL, 2002, INOR 108.
6 J. M. Maher, R. P. Beatty and N. J. Cooper, *Organometallics*, 1985, **4**, 1354–1361.
7 (*a*) J. Kress, M. Wesolek, J.-P. Le Ny and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 1981, 1039–1040; (*b*) R. Dantona, E. Schweda and J. Strähle, *Z. Naturforsch., Teil B*, 1984, **39**, 733–735.
8 Y. Chen, W. Petz and G. Frenking, *Organometallics*, 2000, **19**, 2698–2706.
9 (*a*) M. Etienne, P. S. White and J. L. Templeton, *J. Am. Chem. Soc.*, 1991, **113**, 2324–2325; (*b*) R. L. Miller, P. T. Wolczanski and A. L. Rheingold, *J. Am. Chem. Soc.*, 1993, **115**, 10422–10423; (*c*) S. L. Latesky and J. P. Selegue, *J. Am. Chem. Soc.*, 1987, **109**, 4731–4733; (*d*) W. Beck, W. Knauer and C. Robl, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 318–320.
10 (*a*) P. González-Herrero, B. Weberndörfer, K. Ilg, J. Wolf and H. Werner, *Angew. Chem., Int. Ed.*, 2000, **39**, 3266–3269; (*b*) disorder problems in crystals of $(PPr^i{}_3)_2(OPh)Ru{\equiv}CPh$ prevent an accurate [Ru≡C] bond length determination in this molecule: J. N. Coalter, J. C. Bollinger, O. Eisenstein and K. G. Caulton, *New J. Chem.*, 2000, **24**, 925–927.
11 S.-T. Liu, T.-Y. Hsieh, G.-H. Lee and S.-M. Peng, *Organometallics*, 1998, **17**, 993–995.
12 See references in T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18–29.