Terminal ruthenium carbido complexes as σ-donor ligands‡

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The terminal carbido ligand of (PCy₃)₂(Cl)₂RuC coordinates to other metal centers in a σ-donor fashion, as in (PCy₃)₂(Cl)₂Ru(C≡C–Pd(Cl)₂(SMe₂)) and (PCy₃)₂(Cl)₂Ru≡C–Mo(CO)₅.

In 1995, we reported that the bis(triphenylphosphine)ruthenium benzylidene complex (PPh₃)₂(Cl)₂Ru=C≡CHPh reacts with trans-2,3-dicarbomethoxymethylene cyclopropane to yield a unique 2,3-dicarbomethoxyxycyclopropane carbene complex, (PPh₃)₂(Cl)₂Ru=C(CHCO₂Me)₂ (1). Recent work by Heppert and co-workers, in which they obtain the terminal carbido complex (PCy₃)₂(Cl)₂RuC (2) from the closely related bis(tricyclohexylphosphine) derivative (PCy₃)₂(Cl)₂Ru=C≡CHPh plus trans-2,3-dicarbomethoxymethylencyclopropane, prompted us to re-examine the chemistry of 1.

The addition of at least two equivalents of PCy₃ to 1 causes the instant release of dimethyl fumarate and provides electron-donating PCy₃ ligands are required for olefin elimination, and provides an isolated product yield greater than for the transformation of (PCy₃)₂(Cl)₂RuC (2) (Scheme 1).

‡ (PPh₃)₂(Cl)₂Ru=C≡CHPh

In 1995, we reported that the bis(triphenylphosphine)ruthenium benzylidene complex (PPh₃)₂(Cl)₂Ru=C≡CHPh plus trans-2,3-dicarbomethoxymethylene cyclopropane, 2,002, 2524, provides (PCy₃)₂(Cl)₂RuC (4) (Scheme 1).‡ We initially chose 3 as a coordination partner based on its compact square-planar geometry, but the analogous reaction with octahedral (CO)₅Mo(NMe₃)⁵ is also successful and provides (PCy₃)₂(Cl)₂Ru≡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 PCy₃ ligands and the equatorial tetracarbonyl ‘wall’.

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 (BurCH₃)₂(BrW=O–AlBr₃, and (PMe₂Ph)₂Cl-3Re≡N–BCl₃. 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 nucelophilic ligand with a lone pair available for bonding.‡

Both 4 and 5 are characterized by distinctive ¹³C NMR resonances for the μ-carbido ligands at δ 381.2 and 446.3, respectively. Further downfield shift of 5 likely reflects the weaker carbido–molybdenum interaction in this molecule. In comparison, the ¹³C resonance of the terminal carbido ligand in 2 appears at δ 471.8. 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 that in the N-heterocyclic carbene derivative (H₂I-Mes)(PCy₃)(Cl)₂RuC (H₂I-Mes = 1,3-dimesitylimidazolidine-2-ylidene) [1.650(2) Å]. 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 carbene complex [(PPPh₃)₂(Cl)(CF₃CO₂)₂Ru≡CCH₂Ph][BAr₄] [1.650(4) Å].¹⁰ The palladium–carbon distance in 4 [1.946(2) Å] is similar to that in [(Et₂H₂Im)PdCl(η-C₃H₄)][1.946(3) Å] (Et₂H₂Im = 1,3-dieethylimidazolidine-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 (TPF)(CO)₅Mo≡C–Re(CO)₅(Cp) and (Me₅C₆)₂W≡C–Ru(CO)₂(Cp), although the allylide alternative [M=C–M] is also possible, as in the case of (TTPF)Fe≡C=Re(CO)₅Re(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 (PCy₃)₂(Cl)₂RuC has a somewhat stronger structural trans influence than SMe₂. 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 (H₂I-Mes)(PCy₃)(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 H₂I-Mes ligand.

Previous work has shown that the [(PR₃)₂(Cl)₂Ru] scaffold can be used to isolate ruthenium carbene complexes with a wide variety of substituents,¹² and the discovery that this same

Scheme 1

¹ Electronic supplementary information (ESI) available: additional crystallographic information. See http://www.rsc.org/suppdata/cc/b2/b207903bl

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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 an η-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 Walmont for helpful discussions.

Notes and references

† Synthesis of 2: Under a nitrogen atmosphere, 40.0 mg (0.143 mmol) of PCy3 was added to a solution of 30.1 mg (0.0353 mmol) of 1 in 3 mL CH2Cl2. 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%). 

‡ Crystal data for 2: C84H78Cl2P4Ru2(SMe)2, M = 822.92, monoclinic, space group P21/n (14), α = 9.9605(7), β = 19.737(2), c = 21.505(2) Å, β = 92.128(1)°, V = 4227.3 Å3, T = 98 K, Z = 4, μ(Mo-Kα) = 0.601 mm−1, 62446 measured reflections, 10049 unique, 7579 reflections with I > 2σ(I), all unique used in refinement, final R1 = 0.1132, wR2 = 0.1505.

Crystal data for 3: C31H32Cl6P6S6M, M = 301.56, monoclinic, space group P21/n (#14), a = 8.357(1), b = 5.9396(7), c = 10.065(2) Å, β = 106.321(2)°, V = 479.51(4) Å3, T = 98 K, Z = 2, μ(Mo-Kα) = 2.851 mm−1, 8996 measured reflections, 1125 unique, 1057 reflections with I > 2σ(I), all unique used in refinement, final R1 = 0.0191, wR2 = 0.0390.

Crystal data for 4: C39H34Cl2P2Ru2S2Cl2CH4, 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) Å3, T = 98 K, Z = 2, μ(Mo-Kα) = 0.964 mm−1, 5477 measured reflections, 12240 unique, 10533 reflections with I > 2σ(I), all unique used in refinement, final R1 = 0.0324, wR2 = 0.0523, CCDC 190234, 186048 and 186479. See http://www.rsc.org/suppdata/cb/20/207903fb for crystallographic data in CIF or other electronic format.

5 Heppert and co-workers have reported the related complex [PCy2(η3-C5H4)Ru(η1-μ-C5H4)] 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.