

Communications to the Editor

A Methyl Group Bridging on Three Metal Atoms. Solid-State and Solution Structural Characterization of the $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-CH}_3)(\text{CO})_9]^-$ Anion

T. Beringhelli,* G. D'Alfonso,* M. Panigati, and F. Porta

Dipartimento di Chimica Inorganica
Metallorganica e Analitica e Centro CNR
CSSMTBO, via Venezian 21, 20133 Milano, Italy

P. Mercandelli,* M. Moret, and A. Sironi

Dipartimento di Chimica Strutturale e
Stereochimica Inorganica e Centro CNR
CSSMTBO, via Venezian 21, 20133 Milano, Italy

Received September 22, 1998

Surface methyls have been proposed as intermediates in Fischer–Tropsch synthesis¹ and in methane activation over metals.² Several studies have provided evidence for CH_3 on metal surfaces³ and in most cases vibrational spectroscopies have suggested a C_{3v} symmetry,^{3d–f} either in a top-site or in a 3-fold hollow site. Transition-metal clusters are considered reliable models of the metal surfaces in chemisorption and catalysis⁴ because they offer the possibility of stabilizing unsaturated intermediates through multicenter interactions. However, until now no C_{3v} coordinated methyls were known in cluster chemistry.⁵ The only previous example of a μ_3 -methyl in a triangular cluster,⁶ namely $[\text{Fe}_3(\mu\text{-H})(\mu_3\text{-H}_2\text{CH})(\text{CO})_9]^-$,¹¹ showed agostic interactions lowering the symmetry to C_s . Moreover, this species was detected only by ¹H NMR, due to its thermal instability. The $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-CH}_3)(\text{CO})_9]^-$ anion (**1**) here reported offers, therefore, the first opportunity for a full characterization, in the solid state and in solution, of a methyl group interacting with three transition metals.

The anion **1** is obtained in high yield by reacting the unsaturated anion $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-H})(\text{CO})_9]^-$ ¹² with CH_2N_2 .¹³ The NMR data

(1) (a) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (c) Brady, R. C., III; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181. (d) Bell, A. T. *Catal. Rev.—Sci. Eng.* **1981**, *23*, 203. (e) Baetzold, R. C. *J. Phys. Chem.* **1984**, *88*, 5583.

(2) (a) Pitchai, R.; Klier, K. *Catal. Rev.—Sci. Eng.* **1986**, *28*, 13 and references therein. (b) Lee, M. B.; Yang, Q. Y.; Ceyer, S. T. *J. Chem. Phys.* **1987**, *87*, 2724. (c) Yang, Q. Y.; Johnson, A. D.; Maynard, K. J.; Ceyer, S. T. *J. Am. Chem. Soc.* **1989**, *111*, 8748. (d) Burghgraef, H.; Jansen, A. P. J.; van Santen, R. A. *Surf. Sci.* **1995**, *324*, 345.

(3) (a) Steinbach, F.; Kiss, J.; Krall, R. *Surf. Sci.* **1985**, *157*, 401. (b) Yates, J. T., Jr.; Gates, S. M.; Russel, J. N., Jr. *Surf. Sci.* **1985**, *164*, L839. (c) Kaminsky, M. P.; Winograd, N.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1986**, *108*, 1315. (d) Lee, M. B.; Yang, Q. Y.; Tang, S. L.; Ceyer, S. T. *J. Chem. Phys.* **1986**, *85*, 1693. (e) Yang, Q. Y.; Maynard, K. J.; Johnson, A. D.; Ceyer, S. T. *J. Chem. Phys.* **1995**, *102*, 7734. (f) Bent, B. E. *Chem. Rev.* **1996**, *96*, 1361 and references therein.

(4) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.

(5) Methyl groups capping the triangular faces of Li_4 tetrahedra are present in the “cubane” structure of $(\text{LiMe})_4$: Weiss, E.; Lucken, E. A. C. *J. Organomet. Chem.* **1964**, *2*, 197.

(6) The μ_3 -bridging coordination is much more common⁷ and often involves agostic interactions.⁸ In triangular clusters it has been observed in $[\text{Os}_3(\mu\text{-H})(\mu\text{-HCH}_2)(\text{CO})_{10}]^0$ and in $[\text{Re}_3(\mu\text{-CH}_3)_3(\text{CH}_3)_6(\text{PEt}_2\text{Ph})_2]$.¹⁰

(7) See, for example: Holton, J.; Lappert, M. F.; Pearce, R.; Yarrow, P. I. *W. Chem. Rev.* **1983**, *83*, 135, and references therein.

(8) (a) Brookart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1. (b) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299.

(9) (a) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225.

(b) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7726.

indicate a C_{3v} symmetry of the whole anion,¹⁴ in agreement with the solid-state structure (Figure 1).¹⁶ **1** contains a nearly equilateral metal atom triangle capped by a triple-bridging methyl ligand, with three hydrides bridging the Re–Re edges on the side opposite the μ_3 -methyl ligand. The Re– C_{Me} distance in the triple-bridging methyl complex **1** (mean 2.401 Å) is longer than those found for terminal and double-bridging methyl ligands in $[\text{Re}_3(\mu\text{-CH}_3)_3\text{-}(\text{CH}_3)_6(\text{PEt}_2\text{Ph})_2]$ (mean 2.158 and 2.304 Å, respectively).¹⁰ The methylic hydrogens have been located as eclipsed with respect to the $\text{C}_{\text{Me}}\text{–Re}$ bonds and directed away from the triangular plane. If the methyl group were regarded as a one-electron donor (isobal with hydrogen), the anion **1** would be a “super-unsaturated” species (44 valence electrons), as the $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-H})(\text{CO})_9]^-$ ¹² and $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-AuPPh}_3)(\text{CO})_9]^-$ ¹⁷ anions, requiring formally two double Re–Re bonds, delocalized on the three edges. However, the average Re–Re bond distance in **1** (2.984 Å) is longer than that observed in the AuPPh_3 derivative (2.894 Å)¹⁷ and comparable to those found for the (saturated) species $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-OH})(\text{CO})_9]^-$ (2.979 Å)¹⁸ and $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-O})(\text{CO})_9]^{2-}$ (2.966 Å).¹⁹ This suggests that the methyl ligand should act as a “more-than-one-electron donor”. Theoretical calculations²⁰ have indeed evidenced both σ and π donations²¹ to the cluster moiety,²² the latter giving rise, in the light of its C/H (hence Re/H) bonding character and of the short $\text{Re}\cdots\text{H}$ distances (2.269 Å) and small Re–C–H angles (68.6°), to some degree of agosticity. The title anion can thus be viewed either as a π -stabilized unsaturated species²⁴ or as a saturated one, assuming that the two π orbitals formally donate four electrons.

(10) Edwards, P.; Mertis, K.; Wilkinson, G.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 334.

(11) (a) Dutta, T. K.; Vites, J. C.; Jacobsen, G. B.; Fehlner, T. P. *Organometallics* **1987**, *6*, 842. (b) Vites, J. C.; Jacobsen, G. B.; Dutta, T. K.; Fehlner, T. P. *J. Am. Chem. Soc.* **1985**, *107*, 5563.

(12) (a) Beringhelli, T.; D'Alfonso, G. *J. Chem. Soc., Chem. Commun.* **1994**, 2631. (b) Beringhelli, T.; D'Alfonso, G.; Garavaglia, M. G. *J. Chem. Soc., Dalton Trans.* **1996**, 1771. (c) Horng, H. C.; Cheng, C. P.; Yang, C. S.; Lee, G.-H. *Organometallics* **1996**, *15*, 2543.

(13) A sample of $[\text{PPh}_4][\text{Re}_3\text{H}_4(\text{CO})_9]$ (0.074 mmol) in CH_2Cl_2 was treated at 0 °C with an ethereal solution of CH_2N_2 (1.5 mmol). After 1 h the solution was concentrated, and slow addition of *n*-hexane gave a ocherous precipitate of $[\text{PPh}_4]\text{1}$ (isolated yield 90%). IR, CH_2Cl_2 , $\nu(\text{CO})$: 2007 s, 1919 s cm^{-1} .

(14) ¹H NMR (CD_2Cl_2) δ –6.47 (s, 3H, CH_3), –13.39 (s, 3H, $\mu\text{-H}$) at 298 K; δ –6.49, –13.64 at 193 K. ¹³C NMR (CD_2Cl_2) δ 197.16 (3), 185.23 (6), –73.07 (1) at 298 K; δ 197.53, 185.43, –71.39 at 193 K. The presence of three hydrogens bound to the carbon at –73.07 ppm was first proved through a 2D ¹H–¹³C correlation experiment modified according to Bucher et al.¹⁵ and then confirmed by ¹³C–¹H coupled spectra (quartet, ¹J_{CH} 117.3 Hz at 298 K, 118.0 Hz at 193 K).

(15) Bucher, U. E.; Lengweiler, T.; Nanz, D.; von Philipsborn, W.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 548.

(16) X-ray data (295 K): pale yellow crystals of $[\text{PPh}_4]\text{1}\cdot\text{Et}_2\text{O}$, monoclinic ($P2_1/n$), $a = 14.083(3)$ Å, $b = 12.329(1)$ Å, $c = 23.834(3)$ Å, $\beta = 97.36(1)$, $Z = 4$, $R = 0.0208$, $wR = 0.0463$, $S = 0.942$.

(17) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; De Maldé, V.; Freni, M. *J. Chem. Soc., Chem. Commun.* **1986**, 735.

(18) Beringhelli, T.; D'Alfonso, G.; Freni, M.; Ciani, G.; Molinari, H. *J. Organomet. Chem.* **1986**, *311*, 177.

(19) Ciani, G.; Sironi, A.; Albano, V. G. *J. Chem. Soc., Dalton Trans.* **1977**, 1667.

(20) DFT calculations at the B3LYP level have been done using a double- ζ plus polarization basis set, incorporating relativistic ECP for rhenium atoms (see Supporting Information). Donor–acceptor interactions between CH_3^- and $[\text{Re}_3]$ have been analyzed according to a CDA approach: Dapprich, S.; Frenking, G. *J. Phys. Chem.* **1995**, *99*, 9352.

(21) For a previous suggestion of a CH_3 acting as a π -donor see: Sini, G.; Macgregor, S. A.; Eisenstein, O.; Teuben, J. H. *Organometallics*, **1994**, *13*, 1049.

(22) Here metal-to-methyl back-bonding into C–H antibonding orbitals seems to play a negligible role, at variance with the Ni surface-methyl interaction previously analyzed.²³

(23) Schule, J.; Siegbahn, P.; Wahlgren, U. *J. Chem. Phys.* **1988**, *89*, 6982.

(24) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25.

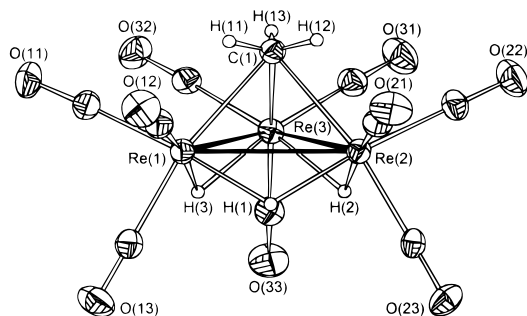
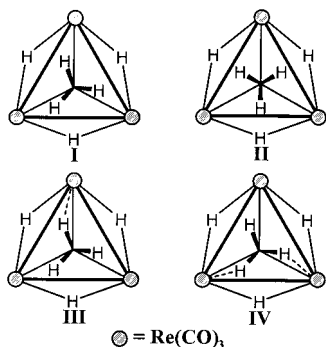


Figure 1. ORTEP drawing of the anion $[\text{Re}_3(\mu\text{-H})_3(\mu_3\text{-CH}_3)(\text{CO})_9]^-$ (**1**) of idealized C_{3v} symmetry. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms were given arbitrary radii. Relevant bond distances (Å): Re(1)–Re(2) 2.9936(2); Re(1)–Re(3) 2.9796(2); Re(2)–Re(3) 2.9778(2); Re(1)–C(1) 2.417(4); Re(2)–C(1) 2.375(4); Re(3)–C(1) 2.411(4).

Chart 1



In solution, the observed C_{3v} symmetry could arise (i) from the presence of a single (static or dynamic) symmetrical tautomer (either the solid-state isomer I, or II in Chart 1); (ii) from the presence of a single unsymmetrical tautomer in which a fast exchange equalizes different hydrogens (either III or IV in Chart 1); (iii) from a fast exchange among different tautomers. The last hypothesis is very unlikely, since the δ and J_{CH} values do not vary significantly from 298 to 193 K¹⁴ (the position of the equilibria should be temperature sensitive). To discriminate between (i) and (ii) we prepared partially deuterated samples of **1** (**1-d**, see Supporting Information), since it is known²⁵ that the preference of deuterium for stiffer bonds results in significant, temperature-dependent, isotope shifts in the presence of fast equilibria among different proton sites.²⁶ In the present case the

(25) Siehl, H.-U. *Adv. Phys. Org. Chem.* **1987**, 23, 63.

(26) Many applications to fluxional agostic systems have been published,⁸ after the first elegant report,⁹ and the observed shifts are on the order of tenths of ppm. See for instance: (a) 340, 390 ppb at 308 K and 550, 680 ppb at 197 K in $[\text{Os}_3(\mu\text{-H})(\mu\text{-HCH}_2)(\text{CO})_{10}]$;^{9b} (b) 290, 270 ppb at 293 K in $[\text{Fe}_3(\mu\text{-H})(\mu_3\text{-H}_2\text{CH})(\text{CO})_9]$;^{11b} (c) 270, 330 ppb at 243 K and 325, 414 ppb at 203 K in $[\text{Re}_2(\mu\text{-H})(\mu\text{-CH}_3)(\text{CO})_8]$.²⁷

$\Delta\delta$ between the resonances of the CH_3 , CH_2D , and CHD_2 isotopomers were small (-35 and -37 ppb at 298 K, of the same order of magnitude of geminal deuterium isotopic effects)²⁸ and slightly decreased with a lowering of the temperature (-25 and -32 ppb at 193 K), instead of showing the increase typical of fluxional systems. We think, therefore, that the unique signal of CH_3 arises from a true C_{3v} symmetry in solution. The solid-state conformer I is preferred over II on the basis of ^1H relaxation measurements performed on **1-d**,²⁹ the pseudopotential density functional calculations,³⁰ and the results of previous computations on methyl adsorption on metal surfaces.³¹ The weakening of the C–H bonds suggested by the $^1J_{\text{CH}}$ value (117.3 Hz)³² is to be ascribed to the C–H bonding character of the methyl orbitals involved in the π donation.³³

The stability of the $\mu_3\text{-CH}_3$ coordination in **1** likely stems from two main factors. The presence of bridging hydrogens on all of the Re–Re interactions prevents the easy reversible C–H oxidative addition, postulated on metals^{3f} and observed in previous examples of clusters bound CH_x fragments.^{9,11} The bridging location of CH_3 and of the hydrides, on the other hand, hampers CH_4 elimination. Investigation to compare the reactivity of **1** with that of surface methyls is in progress.

Acknowledgment. The authors are indebted to Mr. Pasquale Illiano for his skillful acquisition of the NMR data and to a reviewer for his help in the interpretation of our theoretical results.

Supporting Information Available: Details of the NMR characterization, X-ray diffraction structural determination and quantum mechanical calculations (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA983379M

(27) Carlucci, L.; D'Alfonso, G.; Proserpio, D. *Organometallics*, submitted for publication.

(28) See for instance: Bernheim, R. A.; Batiz-Hernandez, H. *J. Chem. Phys.* **1966**, 45, 2261.

(29) Assuming the eclipsed conformation I, the dipolar interaction of the methyl hydrogens with all of the Re atoms nicely accounts for the relaxation rate not provided by the dipolar H–H mechanism (see Supporting Information).

(30) Geometries of the stationary points have been optimized within C_3 symmetry; however, final geometries of both the eclipsed (I) and the staggered (II) structures have C_{3v} symmetry. I corresponds to the minimum energy conformation; II, which is 10.1 kcal mol⁻¹ higher in energy, is likely to be the transition structure for the rotation of the μ_3 -methyl ligand around the $\text{C}_{\text{Me}}\text{-Re}_3$ axis. The conformations showing one (III) or two (IV) agostic interactions are high-energy nonstationary points on the potential energy surface.

(31) (a) Zheng, C.; Apeloig, Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1988**, 110, 749. (b) Yang, H.; Whitten, J. L. *J. Am. Chem. Soc.* **1991**, 113, 6442.

(32) This value is intermediate between the values typical of “3c–2e” agostic interactions (range 60–90 Hz)⁸ and those reported for terminal, not agostic, methyl groups (130–140 Hz, see for instance: Green, J. C.; Payne, M. P. *Magn. Res. Chem.* **1987**, 25, 544).

(33) Vibrational C–H mode softening for CH_3 adsorbed on metal surfaces has often been observed.^{3f} A $\nu(\text{CH})$ value of 2680 cm⁻¹ was measured in ref d, and a value of 2709 has been calculated in ref 23. The unambiguous attribution of the $\nu(\text{C-H})$ modes of **1** is hampered by the presence of the cation and of chlorated solvent. By comparison with **1-d** we can tentatively assign to $\nu(\text{C-H})$ a broad band at 2740 cm⁻¹.