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An Isolable, Oxygen-Coordinated Silver(I) Complex of Dimethyl Diazomalonate: Synthesis and Characterization of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag[OC(OCH_3)]_2CN_2$ (Where Pz = Pyrazolyl)

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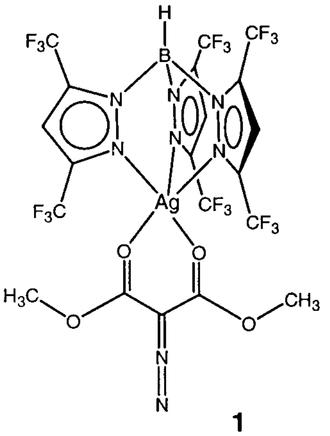
Diazoalkane compounds are excellent starting materials for the preparation of a variety of organic compounds.[1,2] Transition metal ions play an important role as catalysts in most of these reactions.[2−5] For example, a large number of copper and rhodium reagents, including those featuring poly(pyrazolyl)borate ligands,[6−8] are used widely for cyclopropanation and cyclopropenation reactions involving diazo compounds.[2] Silver(I) compounds are among the best catalysts for effecting the Wolff rearrangement of diazoketones to ketenes.[2,9] Diazoalkane reagents are also useful for the synthesis of metal carbene complexes.[3]

Metal adducts containing diazoalkane ligands have also attracted significant interest.[1,3,5,10−13] They are considered as models for key intermediates in reactions involving diazoalkanes and metal ions.[2,3,5,14,15] In this paper, we describe the use of a highly fluorinated tris(pyrazolyl)borate ligand $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$ (where Pz = pyrazolyl)[16] to isolate one such species involving silver(I) and dimethyl diazomalonate.[2,9]

The treatment of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$[17,18] with $N_2C(CO_2CH_3)_2$[19] in hexane resulted in the formation of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag[OC(OCH_3)]_2CN_2$ (**1**) as a colorless, air-stable solid in 89% yield.[20] It is thermally stable up to ca. 90 °C. NMR spectroscopic data are consistent with the formation of a 1:1 adduct. The IR spectrum of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag[OC(OCH_3)]_2CN_2$ exhibited a strong absorption band at 2162 cm^{-1}, corresponding to the N−N stretching mode of the coordinated $N_2C(CO_2CH_3)_2$. Interestingly, this ν_{NN} value is higher than that reported for the free ligand (2137 cm^{-1}).[21] The $\nu_{C=O}$ band of the silver adduct appears at a value (1736 cm^{-1}) lower than the $\nu_{C=O}$ of the free ligand (1764 cm^{-1}). A manganese(I) adduct containing the $N_2C(CO_2CH_3)_2$ ligand, $(\eta^5\text{-}C_5H_5)Mn(CO)_2[N_2C(CO_2CH_3)_2]$, is known (**2**), and it shows ν_{NN} and $\nu_{C=O}$ bands at 1911 cm^{-1} and 1691, 1650 cm^{-1}, respectively.[22] These IR data suggest that Ag(I) and Mn(I) have very different effects on the $N_2C(CO_2CH_3)_2$ ligand.



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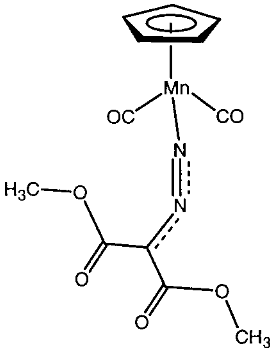

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In order to establish the coordination mode of the diazo molecule, the X-ray crystal structure of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag[OC(OCH_3)]_2CN_2$ was determined.[23] As evident from the ORTEP diagram illustrated in Figure 1, the dimethyl diazomalonate ligand coordinates to silver via carbonyl oxygen atoms. The metal center is five coordinate and adopts a distorted trigonal bipyramidal geometry. The CNN moiety is linear (179.5(6)°). The N−N distance of 1.108(6) Å is short and is at the short end of the typical NN distances for free diazo ligands (1.11−1.13 Å).[22] For comparison, the NN distance of N_2 is 1.0976(2) Å.[24]

In contrast to $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag[OC(OCH_3)]_2CN_2$, the manganese adduct $(\eta^5\text{-}C_5H_5)Mn(CO)_2[N_2C(CO_2CH_3)_2]$ features a N-bonded diazo ligand with a bent CNN moiety (150.5(4)°) and a relatively long N−N bond (1.165(2) Å). The shorter N−N

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(1) Regitz, M.; Maas, G. *Diazo Compounds: Properties and Synthesis*; Academic Press: New York, 1986.
(2) Doyle, M. P.; McKervey, M. A.; Ye, T. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*; Wiley: New York, 1998.
(3) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 800.
(4) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science: California, 1987.
(5) Mizobe, Y.; Ishii, Y.; Hidai, M. *Coord. Chem. Rev.* **1995**, *139*, 281.
(6) Pêrez, P. J.; Brookhart, M.; Templeton, J. L. *Organometallics* **1993**, *12*, 261.
(7) Brunner, H.; Singh, U. P.; Boeck, T.; Altmann, S.; Scheck, T.; Wrackmeyer, B. *J. Organomet. Chem.* **1993**, *443*, C16.
(8) Keyes, M. C.; Chamberlain, B. M.; Caltagirone, S. A.; Halfe, J. A.; Tolman, W. B. *Organometallics* **1998**, *17*, 1984.
(9) Meier, H.; Zeller, K.-P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32.
(10) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 1918.
(11) Curtis, M. D.; Messerle, L.; D'Errico, J. J.; Butler, W. M.; Hay, M. S. *Organometallics* **1986**, *5*, 2283.
(12) D'Errico, J. J.; Messerle, L.; Curtis, M. D. *Inorg. Chem.* **1983**, *22*, 849.
(13) See also for related metal diazo complexes: Sutton, D. *Chem. Rev.* **1993**, *93*, 995.
(14) Hidai, M.; Ishii, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 819−831.
(15) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919.
(16) Dias, H. V. R.; Jin, W.; Kim, H.-J.; Lu, H.-L. *Inorg. Chem.* **1996**, *35*, 2317.
(17) Dias, H. V. R.; Jin, W. *Inorg. Chem.* **1996**, *35*, 267.
(18) Dias, H. V. R.; Jin, W.; Wang, Z. *Inorg. Chem.* **1997**, *36*, 6205.
(19) Peace, B. W.; Carman, F.; Wulfman, D. S. *Synthesis* **1971**, 658.
(20) $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$ (0.15 g, 0.189 mmol) and $N_2C(CO_2CH_3)_2$ (0.03 g, 0.189 mmol) were combined in hexane and stirred overnight. Hexane was removed under reduced pressure to obtain $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag[OC(OCH_3)]_2CN_2$ as a colorless solid, 0.15 g, 89% yield. It was recrystallized from warm hexane at −20 °C. Mp: 90 °C dec. ^1H NMR (C_6D_6): δ 3.27 (s, CH_3, 6H), 6.27 (s, CH, 3H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 51.5 (s, CH_3), 106.6 (s, CH), 119.5 (q, $^1J(C,F)$ = 272 Hz, CF_3), 120.5 (q, $^1J(C,F)$ = 270 Hz, CF_3), 140.3 (q, $^2J(C,F)$ = 44 Hz, CCF_3), 143.3 (q, $^2J(C,F)$ = 38 Hz, CCF_3), 160.7 (s, C=O). ^{19}F NMR (C_6D_6): δ −58.9 (d, $^5J(F,H)$ = 3.2 Hz), −61.6. IR (Nujol), cm^{-1}: 3144, 2668, 2162, 1739, 1556, 1261, 1149, 1107, 1078, 1041, 985, 846, 821, 780, 768. Satisfactory C, H, N.
(21) Regitz, M. *Chem. Ber.* **1966**, *99*, 3128.
(22) Herrmann, W. A.; Kriechbaum, G.; Ziegler, M. L.; Wulknitz, P. *Chem. Ber.* **1981**, *114*, 276.
(23) Crystal data: $C_{20}H_{10}N_8AgBF_{18}O_4$, monoclinic, $P2_1/n$, a = 8.9306(15) Å, b = 25.385(2) Å, c = 14.011(2) Å, β =102.550(18)°, V = 3100.6(8) $Å^3$, Z = 4, D_{calc} = 1.900 g cm^{-3}, T = 298(2) K, GOF = 1.035, R1 = 0.0343 and wR2 = 0.0752 (for $I > 2\sigma(I)$).
(24) Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; John Wiley & Sons: New York, 1972.

10.1021/ic0002521 CCC: $19.00

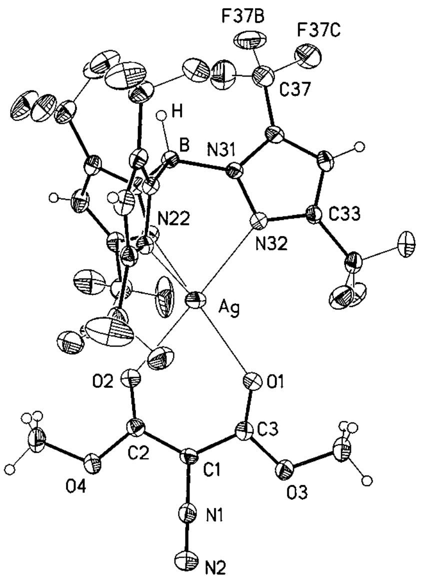

Figure 1. Molecular structure of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag[OC(OCH_3)]_2CN_2$. Selected bond distances (Å) and angles (deg): Ag−O1 2.390(3), Ag−O2 2.434(3), Ag−N22 2.412(3), Ag−N32 2.422(3), Ag−N12 2.454(3), N1−N2 1.108(6), N1−C1 1.336(6), O1−C3 1.210(5), O2−C2 1.195(5), C1−C2 1.448(6), C1−C3 1.449(6); O1−Ag−N22 139.06(11), O1−Ag−N32 106.74(10), N22−Ag−N32 82.38(11), O1−Ag−O2 74.46(10), N22−Ag−O2 99.91(11), N32−Ag−O2 175.00(11), O1−Ag−N12 138.53(11), N22−Ag−N12 82.20(11), N32−Ag−N12 77.32(11), O2−Ag−N12 98.53(11), N2−N1−C1 179.5(6), C3−O1−Ag 132.5(3), C2−O2−Ag 131.6(3), N1−C1−C2 117.1(4), N1−C1−C3 116.5(4), C2−C1−C3 126.5(4), O2−C2−O4 124.1(4), O2−C2−C1 124.8(4), O4−C2−C1 111.1(4), O1−C3−O3 124.4(4), O1−C3−C1 124.6(4), O3−C3−C1 111.0(4).

distance in the silver adduct is consistent with the relatively higher ν_{NN} value. The C═O bond distances of the Ag(I) adduct (1.195(5), 1.210(5) Å) are shorter compared to the typical C═O distance of metal diketonates (1.270 Å).[25] Overall, structural data indicate only very minor changes to the dimethyl diazomalonate ligand upon coordination to silver(I). This is in sharp contrast to the manganese adduct, $(\eta^5\text{-}C_5H_5)Mn(CO)_2[N_2C(CO_2CH_3)_2]$.

Metal complexes with diazoalkane ligands show a diverse range of coordination modes.[1,3,4,13] However, most of these feature bonds between the metal ion and diazo nitrogen atoms. Interestingly, $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag[OC(OCH_3)]_2CN_2$ adopts a sterically more crowded five-coordinate geometry with Ag−O bonding instead of a Ag−η^1-N bonded tetrahedral structure as in $[HB(3,5\text{-}(CF_3)_2Pz)_3]AgNCBu^t$.[18] One possible explanation for this mode of bonding involves the extra stability due to the chelate effect.[26] The metal−η^1-N mode of bonding, although preferred for π-back-bonding metal ions (e.g., Mn(I)),[22] is not particularly advantageous for poor π-donor metals like silver.[18]

In summary, this paper describes the isolation of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag[OC(OCH_3)]_2CN_2$ that features an essentially unperturbed diazoalkane moiety with Ag−O (rather than Ag−N) interactions. The stability of complexes such as $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag[OC(OCH_3)]_2CN_2$ suggests that metal−oxygen bonded species may also play an important role in metal-mediated activation of diazomalonates and other diazoketones.[2,9]

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag[OC(OCH_3)]_2CN_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(26) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1999; p 27.