Transfer of the Carbyne Ligand to the C≡C Bond *versus* Alkyne–Carbyne–CO Coupling in the Reactions of $[(\eta^5\text{-}C_5H_5)(CO)_2Mn{\equiv}CPh]^+$ with Electron-rich Alkynes

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The carbyne cation $[(\eta^5\text{-}C_5H_5)(CO)_2Mn{\equiv}CPh]^+$ **1** reacts with bis(diorganylamino)acetylenes by transfer of the carbyne ligand to the C–C bond of the alkynes to give cyclopropenyl cations; in contrast, the reaction with diorganylaminopropyne affords novel η^4-carbene complexes by regioselective coupling of the carbyne and one CO ligand with the alkyne.

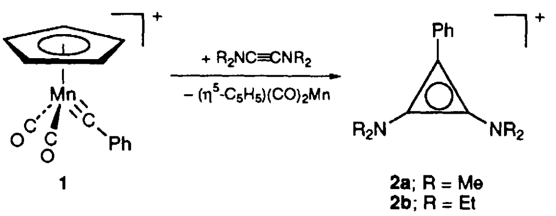
Transition metal carbene complexes have found numerous applications in synthetic organic chemistry through a number of carbene transfer and cycloaddition reactions.[1] Prominent examples are the reactions of carbene complexes with alkynes, alkenes and imines to give naphthol derivatives, cyclopropanes and β-lactams, respectively. In contrast, much less is known about potential applications of carbyne complexes for the synthesis of carbo- and hetero-cycles.[2] Until now, carbyne complexes have been mainly employed as building blocks for the synthesis of transition metal clusters.[3] The intramolecular coupling of carbyne ligands with CO or isocyanide ligands has also been studied in detail.[4] However, the number of studies of the reactivity of carbyne complexes towards *e.g.* alkynes is rather limited. Mayr *et al.* reported the formation of a metallacyclopentadienone and an η^3-oxo cyclobutenyl tungsten complex from $Cl(PMe_3)_3(CO)W{\equiv}CPh$ and phenylacetylene *via* an alkylidyne alkyne intermediate.[5] Dinuclear complexes containing either a bridging C_3R_3 or $C_3H_3C(O)$ ligand are obtained from the reaction of *trans*-$(CO)_4Co–(CO)_4W{\equiv}CR$ with alkynes.[6] The incorporation of the carbyne ligand into the organic substrate and the formation of 9-vinylphenanthrenes is observed in the reaction of *trans*-$Br(CO)_4W{\equiv}CMe$ with 1-alkynyl-1′-vinylbiphenyl,[7] and naphthol complexes are formed when $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}C(C_6H_4Me)$ is protonated in the presence of alkynes and CO by a pathway involving the initial formation of a carbene complex.[8] We now report (*i*) the first transfer of an electrophilic carbyne ligand to the carbon–carbon triple bond of alkynes to give cyclopropenyl cations and (*ii*) the formation of unusual η^4-(1-butadienyl-4-one)carbene and η^4-(1-penta-1,3,4-trienyl) carbene complexes from ynamines and a cationic carbyne complex.

The cationic carbyne complex **1**-BF_4 reacts with bis(dimethylamino)acetylene and bis(diethylamino)acetylene in dichloromethane, even at −50 °C, within seconds to give the cyclopropenium salts **2a**-BF_4 and **2b**-BF_4, respectively (Scheme 1). After removal of the solvent and recrystallization from water or acetonitrile–diethyl ether **2a**·BF_4 and **2b**·BF_4 are obtained as colourless needles in *ca.* 60% yield. The C_5Me_5-analogue of **1**-BF_4, $[(\eta^5\text{-}C_5Me_5)(CO)_2Mn{\equiv}CPh]BF_4$, reacts with bis(diorganylamino)acetylenes in a similar way. Complexes **2a**·BF_4 and **2b**·BF_4 were characterized by elemental analyses and by spectroscopic means.†

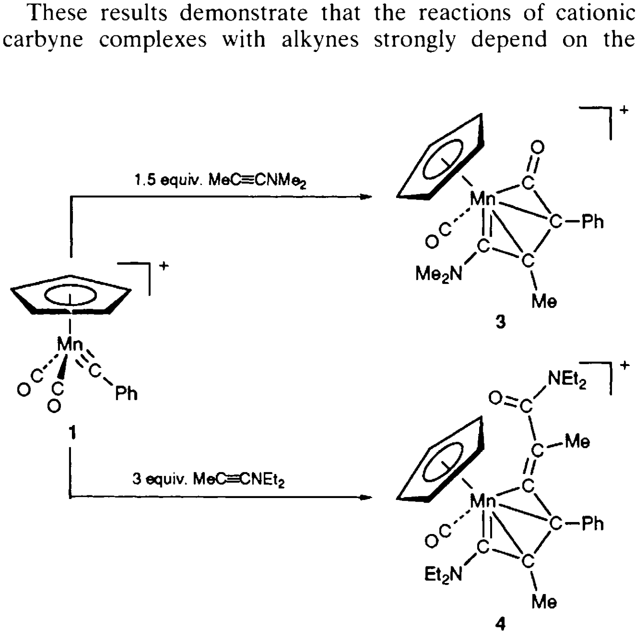
The formation of the cyclopropenyl cations **2**, which is related to the cyclopropanation of olefins by electrophilic carbene complexes,[9] can be explained by a [2 + 2] cycloaddition of the C≡C bond to the Mn≡C bond to give a mangana(III)cyclobutadiene, with subsequent reductive elimination of **2**, as well as by direct addition of the C≡C π bond to the carbyne carbon atom. The latter process seems more likely since cyclopropenyl formation requires non-polar bis(π-donor) substituted alkynes as substrates: when polar dimethylaminopropyne is employed, instead of bis(dimethylamino)acetylene, the reaction takes a different course. Regioselective coupling of the alkyne with the carbyne and a CO ligand of **1**·BCl_4 affords the novel cationic metallacyclic η^4-amino(1-butadienyl-4-one)carbene complex **3** (Scheme 2). After work-up with $HPF_6–H_2O$ and recrystallization from acetone, **3** is isolated as the orange PF_6^- salt in 62% yield. In **3** the CO group bridges the former manganese–carbyne carbon bond. The formation of the isomer of **3** with an inverse arrangement of NMe_2 and Ph (CO bridging the Mn–$CNMe_2$ bond) has not been observed. When solution of **1**·BCl_4 are treated with a threefold excess of diethylaminopropyne the cationic complex **4** is formed (Scheme 2). Complex **4** is derived from the NEt_2 derivative of **3** by [2 + 2] cycloaddition of the ynamine to the bridging CO group and electrocyclic ring-opening. The structures of **3** and **4** were determined by spectroscopic means.‡ In addition an X-ray analysis was carried out on **4**. Although the crystals were of poor quality, the substitution pattern (NEt_2 bonded to the manganese-bound carbon and Ph adjacent to the bridging CO group) is unambiguously established.

The reaction leading to **3** and **4** very likely proceeds by a nucleophilic attack of the ynamine *via* the C(Me) atom at the carbyne carbon, formation of a metallacyclobutadiene and simultaneous or subsequent coupling of a terminal CO ligand with the C(Ph) atom. An alternative, although less likely mechanism involves coupling of the carbyne and a CO ligand to give a η^2-ketenyl complex, which is then trapped by the alkyne.[4] Thus the pathways to **2** and **3**/**4** probably differ already in the initial reaction step.

These results demonstrate that the reactions of cationic carbyne complexes with alkynes strongly depend on the



Scheme 1



Scheme 2

substituents giving either alkyne–carbyne or alkyne–carbyne–CO coupling products and that three-membered carbocycles can be prepared from electrophilic carbyne complexes and alkynes. Recently, imidazolium compounds have been obtained by a head to tail cyclization of two molecules of diorganylcyanamide and the carbyne ligand of **1**.[10]

Financial support of this work by the Government of Baden-Württemberg (Schwerpunkt 'Metallzentrierte Substrattransformationen') and the Fonds der Chemischen Industrie is gratefully acknowledged.

Received, 1st October 1993; Com. 3/05905G

Footnotes

† *Selected data* for **2a**·BF_4: mp 234 °C; ^1H NMR (CD_3CN) δ 3.26 (s, NMe), 3.40 (s, NMe), 7.5–7.7 (m, Ph); ^{13}C NMR (CD_3CN) δ 43.57 (NMe), 43.63 (NMe), 106.77 (*C*Ph), 122.23 (*C*NMe_2), 130.50, 131.02, 132.25, 134.66 (Ph).

For **2b**·BF_4: mp 111 °C; ^1H NMR (CD_3COCD_3) δ 1.42 (t, *J* 7.3 Hz, Me), 1.44 (t, *J* 7.3 Hz, Me), 3.67 (1, *J* 7.3 Hz, NCH_2), 3.80 (q, *J* 7.3 Hz, NCH_2), 7.5–7.8 (Ph); ^{13}C NMR (CD_3COCD_3) δ 14.49 (Me), 14.60 (Me), 48.77 (NCH_2), 49.41 (NCH_2), 107.15 (*C*Ph), 122.59 (*C*NEt_2), 130.54, 130.59, 131.99, 133.49 (Ph).

‡ *Selected data* for **3**·PF_6: mp 145 °C; IR (KBr) 2014 s, 1737 m cm^{-1}; ^1H NMR (CD_3COCD_3) δ 2.54 (CMe), 4.07 (NMe), 4.11 (NMe), 5.63 (η^5-C_5H_5), 7.5–7.7 (Ph); ^{13}C NMR (CD_3COCD_3) δ 16.35 (CMe), 43.77 (NMe), 47.42 (NMe), 51.71 (*C*Ph), 73.44 (*C*Me), 92.72 (η^5-C_5H_5), 129.76, 131.53, 132.40 (Ph), 218.01 [Mn–C(=O)–], 223.36 (CO), 230.68 (*C*NMe_2).

For **4**·PF_6: mp 129 °C; IR (KBr) 1994 s, 1640 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15, 1.25, 1.32, 1.44 (t, *J* 7.0 Hz, CH_2*Me*), 1.81 (CMe), 2.28, (=CMe), 3.11, 3.28, 3.67, 3.98, 4.10, 4.29 (m, NCH_2), 5.14 (η^5-C_5H_5), 7.4–7.5 (m, Ph); ^{13}C NMR (CD_3COCD_3) δ 12.70, 13.78, 14.13, 14.29 (CH_2*Me*), 18.55 (CMe), 22.12 (=C*Me*), 38.84, 43.01, 52.02, 55.67 (NCH_2), 64.64 (*C*Ph), 79.22 (*C*Me), 91.09 (η^5-C_5H_5), 92.11 (MnC=), 129.69, 131.27, 135.26, 137.88 (Ph), 166.17 (=*C*Me), 171.28 [–C(O)–], 224.23 (CO), 228.95 (*C*NEt_2).

References

1 K. H. Dötz in *Transition Metal Carbene Complexes*, ed. K. H. Dötz, H. Fischer, P. Hofmann, F. R. Kreissl, U. Schubert and K. Weiss, Verlag Chemie, Weinheim, 1983, p. 191; K. H. Dötz, *Angew. Chem.*, 1984, **96**, 573; *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 587; R. Aumann, *Angew. Chem.*, 1988, **100**, 1512; *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1456; W. D. Wulff in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, vol. 5, p. 1065; L. S. Hegedus, R. Imwinkelried, M. Alarid-Sargent, D. Dvorak and Y. Satoh, *J. Am. Chem. Soc.*, 1990, **112**, 1109 and references cited therein.

2 See *e.g.* H. P. Kim and R. J. Angelici, *Adv. Organomet. Chem.*, 1987, **27**, 51; *Carbyne Complexes*, ed. H. Fischer, P. Hofmann, F. R. Kreissl, R. R. Schrock, U. Schubert and K. Weiss, VCH, Weinheim, 1988; A. Mayr and H. Hoffmeister, *Adv. Organomet. Chem.*, 1991, **32**, 227.

3 See *e.g.* F. G. A. Stone, *Pure and Appl. Chem.*, 1986, **58**, 529.

4 A. Mayr and C. H. Bastos, *Progr. Inorg. Chem.*, 1992, **40**, 1.

5 A., Mayr, K. S. Lee and B. Kahr, *Angew. Chem.*, 1988, **100**, 1798; *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1730.

6 I. J. Hart, J. C. Jeffery, M. J. Grosse-Ophoff and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1988, 1867; I. J. Hart and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1988, 1899.

7 T. M. Sivavec, T. J. Katz, M. Y. Chiang and G. X.-Q. Yang, *Organometallics*, 1989, **8**, 1620.

8 K. E. Garrett, J. B. Sheridan, D. B. Pourreau, W. C. Feng, G. L. Geoffroy, D. L. Staley and A. L. Rheingold, *J. Am. Chem. Soc.*, 1989, **111**, 8383; K. E. Garrett, W. C. Feng, H. Matsuzaka, G. L. Geoffroy and A. L. Rheingold, *J. Organomet. Chem.*, 1990, **394**, 251.

9 For recent reviews see: M. Brookhart and W. B. Studabaker, *Chem. Rev.*, 1987, **87**, 411; M. P. Doyle, *Chem. Rev.*, 1986, **86**, 919.

10 H. Fischer and C. Troll, *Chem. Ber.*, 1993, **126**, 2373.