Preliminary Communication

Nucleophilic cyclocarbenes as ligands in metal halides and metal oxides *

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Abstract

The nucleophilic cyclocarbene 1,3-dimethylimidazolin-2-ylidene (1) reveals universal ligand properties in metal coordination chemistry: in addition to the well-known stabilization of low oxidation-state transition metal fragments, this particular class of carbenes also coordinates with metal halides and metal oxides thus resembling the properties of conventional ether (O), amine (N), and phosphane (P) ligands. Complexes of titanium(IV), zirconium(IV), hafnium(IV), vanadium(II), niobium(IV), tantalum(IV) of general formula MX_nL_m (3a–f) and the rhenium(VII) of formula $CH_3ReO_3L_2$ (3g) are reported (L = 1,3-dimethylimidazolin-2-ylidene).
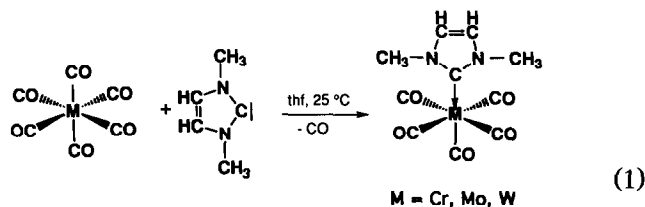
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1. Introduction

Cyclocarbenes derived from imidazolium and pyrazolium salts have been well-known ligands in organometallic chemistry, represented particularly by low-valent transition metal complexes [2,3]. Thus the nucleophilic carbene 1,3-dimethylimidazolin-3-ylidene (1) can be introduced into metal carbonyl complexes from both the (indefinitely stable) imidazolium precursor salts according to the work of Öfele et al. [3] and the (less stable) free carbenes (Eq. (1)) [4]. These latter compounds have become available through the work of Arduengo et al. [5].

$$ \text{(1)} $$

M = Cr, Mo, W

We have recently shown that this class of heterocyclic carbenes has ligand properties comparable to those of electron-rich phosphanes [4]. This similarity suggests future applications of such ligands in organometallic homogeneous catalysis. We have in the meantime observed a much broader application of imidazolium-derived carbenes, for which reason we now disclose typical examples of high oxidation-state metal complexes containing carbene ligands of type 1.

Treatment of metal halides such as $TiCl_4 \cdot (thf)_2$ (2a), $ZrCl_4 \cdot (thf)_2$ (2b), $HfCl_4 \cdot (thf)_2$ (2c), $VCl_2 \cdot (tmeda)_2$ (2d), $NbCl_4 \cdot (py)_2$ (2e), $TaCl_4 \cdot (py)_2$ (2f), and of the oxide CH_3ReO_3 (2g) dissolved in completely dry tetrahydrofuran, with the free carbene 1 in the proper molar ratio yields precipitates 3a–g that constitute simple substitution products (Scheme 1). The compounds are of poor solubility in unpolar solvents. They dissolve well in polar solvents like CH_3CN or CH_2Cl_2. 3a–g contain the C-coordinated carbene in place of the previous tetrahydrofuran (thf), pyridine (py) or N,N,N',N'-tetramethyl-ethylendiamine (tmeda) ligands. Elemental analyses and spectra clearly prove the simple composition and the conventional structures of this easily available new classes of coordination compounds that derive from well-known metal halides and metal oxides (Tables 1 and 2).

We particularly note that the free carbene 1 displaces O- and N-donor ligands (thf, py, and tmeda, resp.) that are normally used to prevent the corresponding metal halides and oxides from further nucle-
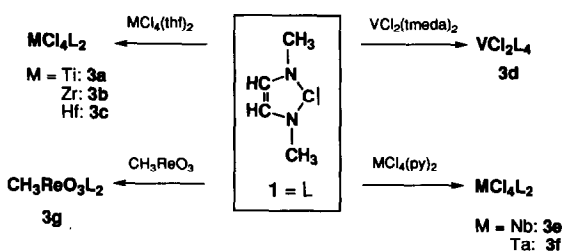
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* Communication 139 on Multiple Bonds between Main-Group Elements and Transition Metals. For Communication 138 see ref. 1.

Scheme 1.

TABLE 1. Elemental analyses of the carbene complexes 3a–f

	Calculated				Found			
	C	H	N	Cl	C	H	N	Cl
3a [a]	31.45	4.22	14.67	37.13	31.22	4.32	14.20	36.52
3b	28.24	3.79	13.17	33.34	27.68	3.99	12.61	32.94
3c	23.43	3.15	10.93	27.67	24.15	3.39	10.99	27.17
3d	47.44	6.37	22.13	14.00	47.15	6.52	21.92	13.66
3e	28.13	3.78	13.12	33.21	28.46	3.63	12.86	32.87
3f	23.32	3.13	10.88	27.53	23.72	3.31	10.38	27.13

[a] Found: Ti, 12.05, calc.: 12.54.

TABLE 2. NMR data of the carbene complexes 3a–c at 25°C

NMR	^{1}H(δ, ppm, CD_3CN)		^{13}C(δ, ppm, CD_3CN)		
	N–CH$_3$	Imid.-H	N–CH$_3$	Imid.-C	Carbene-C
3a [a]	3.85 s	7.34 s	36.6	124.2	180.7
3b	3.82 s	7.32 s	36.3	124.6	178.2
3c	3.83 s	7.33 s	36.6	124.3	176.2

[a] Addition of water generates the imidazolium cation (δCH = 140.30 ppm, CD_3CN).

ation (e.g. oligomerization) and to enhance their stability for hydrolysis.

The new compounds 3a–f [1] very much resemble the precursor compounds 2a–f in colour, thermal stability and molecular structures [6]. They are very sensitive to air and moisture. Dissociation occurs under the conditions of electron-impact mass spectrometry.

In the case of 2g (Scheme 1), the nucleophilic free carbene 1 adds to the electron-deficient, coordinatively unsaturated metal center without displacing another ligand. 3g forms as a yellow solid which is sensitive to air and temperature. If the compound is warmed to −20°C, methane eliminates (GC/MS). The methane originates from the metal-coordinated methyl groups as shown by deuterium labeling experiments. Elemental analyses as well as IR- and NMR data give sufficient evidence for a hexacoordinate bis(carbene) complex very much ressembling amine complexes of the type $CH_3ReO_3 \cdot L_2$ (L'_2 = bipyridine [10,11]). The ^{13}C signal of the "carbenoid", metal-coordinated carbon atom shows up at $\delta = 176.7$ ppm (CD_3CN) which chemical shift compares well with conventional carbene complexes, e.g. $Re(L)_2I(CO)_3$ ($\delta C = 175.1$ ppm [7]). While the starting compound CH_3ReO_3 2g exhibits a ^{17}O signal at $\delta = 829$ ppm ($CDCl_3$), the new carbene-"adduct" (σ-donor coordination) is recorded

at $\delta = 728$ ppm. Comparison of the pronounced high-field shift of the ^{17}O resonance of 3g with the data of related adducts (pyridine [8], quinuclidine [9], 2,2'-bipyridine [10]) once again gives evidence of the extensive σ-donor of type-1 carbenes [4].

Re_2O_7 reacts instantaneously with 1. However, reduction of Re(VII) occurs in this particular case. The violet, insoluble product has so far escaped characterization. A cyclovoltammetric study confirmed that Re_2O_7 and 1 undergo a redox reaction with concomitant formation Re(VI) [12].

Our results show that nucleophilic carbenes of type 1 are sufficiently flexible in their electronic structure for them to adopt metal species ranging from electron-rich fragments, e.g. metal carbonyls, to Lewis-acidic high oxidation-state compounds such as metal halides and metal oxides. The carbene ligand seems to have a low tendency to react with the halide and oxide ligands. By way of contrast, standard phosphanes (such as triphenylphosphane) eliminate an oxygen ligand from CH_3ReO_3 (2g) to yield phosphane oxides; reduction of the metal ($Re^{VII} \rightarrow Re^V$) occurs at the same time [13]. Further work is in progress to explore applications and advantages of carbenes in comparison to conventional donor ligands in high-valent metal complexes.

[1] Meanwhile carbene complexes of Au(I) and Cu(I) of general formula Cl–ML have been synthesized (M. Elison, Ph.D. Thesis, in preparation). The Cu(I) complex is related to the ionic derivative [L'_2Cu][CF_3SO_3] with $L' = 1,3$-dimesitylimidazolyl-2-ylidene [5g].

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2. Experimental details

All experiments have been carried out by using standard Schlenk techniques and completely dry solvents (water content < 1 ppm; Karl–Fischer titrations). Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer, the NMR spectra on a FT-Jeol GX 400 instrument. All NMR solvents were "freeze–pump–thaw" degassed and stored over molecular sieves before use. Elemental analyses were performed in the Microanalytical Laboratory of our Institute. The starting materials 2a–g were prepared according to published procedures [6,11]. δ-values (NMR) are given in ppm. The standard for ^{17}O NMR spectra was $\delta(H_2O) = 0.0$ ppm.

2.1. Carbene complexes 3a–f

Two (four) equivalents of 1 (20 mmol) are added successively to a stirred solution of 10 mmol of MCl_4D_2 (M = Ti, Zr, Hf, Nb, Ta; D = thf, py) or VCl_2 (tmeda)$_2$ in thf (20 ml). Coloured precipitates of 3a–f are formed after a few seconds. They are successively washed with 30 ml of thf, 30 ml of Et_2O and 30 ml of n-hexane. The products are finally dried in an oil-pump vacuum. 3a–3f are brown or yellow, air- and moisture sensitive powders. Elemental analyses and NMR spectra are summarized in Tables 1 and 2 respectively.

2.2. Bis(1,3-dimethylimidazolyl-2-ylidene)methyltrioxo-rhenium(VII) (3g)

0.60 g (2.41 mmol) of 2g are dissolved in 10 ml of thf. The solution is cooled to −60°C. 0.46 g (4.81 mmol) of 1 are then added. A yellow precipitate 3g forms after a few seconds. It is washed with 30 ml of thf and 30 ml of Et_2O. The yellow residue is finally dried in an oil-pump vacuum. Yield: 0.86 g (81%). The compound decomposes slowly at −35°C in the solid state.

IR (CH_3CN): 1664 m, 1653 m ν(C–N), 935 s ν(Re–O), 3104 m, 2949m ν(Re–CH_3). −^1H NMR (CD_3CN, −60°C): δ = 6.90 s (imid. – H, 4H), 3.52 s (CH_3, 12H), 2.40 s (Re–CH_3, 3H). −^{13}C NMR (CD_3CN, −60°C): δ = 176.7 (carbene-C), 122.71 (NCHCHN), 37.05 (CH_3-N), 25.81 (Re–CH_3). −^{17}O NMR ($CDCl_3$,

−60°C): δ = 728. Elemental analysis: calc.: C, 29.93, H, 4.34, Re, 42.17, found: C, 30.44, H, 4.29, Re, 42.16.

References

1 S. Genin, R. Hoffmann, W.A. Herrmann and R.W. Fischer, J. Am. Chem. Soc., submitted.

2 Reviews: (a) F.P. Pruchnik, Organometallic Chemistry of the Transition Elements, Plenum Press, New York, 1990, pp. 277–326; (b) K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kreißl, U. Schubert and H. Weiss (eds.), Transition Metal Carbene Complexes, Verlag Chemie, Weinheim, 1983; (c) D.J. Cardin, B. Cetinkaya and M.F. Lappert, Chem. Rev., 72 (1972) 545; (d) A. Haaland, A. Hammel, K. Rypdal and H.V. Volden, J. Am. Chem. Soc., 112 (1990) 4547.

3 (a) K. Öfele, J. Organomet. Chem., 12 (1968) P42; (b) K. Öfele and C.G. Kreiter, Chem. Ber., 105 (1972) 529; (c) K. Öfele and M. Herberhold, Z. Naturforsch., Teil B, 28 (1973) 306; (d) C.G. Kreiter, K. Öfele and G.W. Wieser, Chem. Ber., 109 (1976) 1749; (e) K. Öfele and M. Herberhold, Angew. Chem., 82 (1970) 775; Angew. Chem., Int. Ed. Engl., 9 (1970) 739; (f) K. Öfele, E. Roos and M. Herberhold, Z. Naturforsch., Teil B, 31 (1976) 1070.

4 K. Öfele, W.A. Herrmann, D. Mihalios, M. Elison, E. Herdtweck, W. Scherer and J. Mink, J. Organomet. Chem., 459 (1993) 177.

5 (a) A.J. Arduengo III, R.L. Harlow and M. Kline, J. Am. Chem. Soc., 113 (1991) 361; (b) D.A. Dixon and A.J. Arduengo III, J. Phys. Chem., 95 (1991) 4180; (c) A.J. Arduengo III, M. Kline, J.C. Calabrese and F. Davidson, J. Am. Chem. Soc., 113 (1991) 9704; (d) A.J. Arduengo III, H.V.R. Dias, R.L. Harlow and M. Kline, J. Am. Chem. Soc., 114 (1992) 5530; (e) A.J. Arduengo III, H.V.R. Dias, J.C. Calabrese and F. Davidson, J. Am. Chem. Soc., 114 (1992) 9724; (f) A.J. Arduengo III, H.V.R. Dias, J.C. Calabrese and F. Davidson, Inorg. Chem., 32 (1993) 1541; (g) A.J. Arduengo III, H.V.R. Dias, J.C. Calabrese and F. Davidson, Organometallics, 12 (1993) 3405; (h) A.J. Arduengo III, H.V.R. Dias, F. Davidson and R.L. Harlow, J. Organomet. Chem., 462 (1993) 13; (i) H.V.R. Dias and W. Jin, Tetrahedron Lett., 35 (1994) 1365.

6 (a) R.E. McCarley and J.C. Boatman, Inorg. Chem., 2 (1963) 547; (b) R.E. McCarley and B.A. Torp, Inorg. Chem., 2 (1963) 540; (c) L.E. Manzer, Inorg. Synth., 21 (1982) 135; (d) J.J.H. Edema, W. Stauthamer, F. van Bolhuis, S. Gambarotta, W.J.J. Smeets and A.L. Spek, Inorg. Chem., 29 (1990) 1302.

7 D. Mihalios, Ph. D. Thesis, Technische Universität München, 1992, p. 95.

8 W.A. Herrmann, P.W. Roesky, R. Alberto, G. Artus and unpublished results W. Scherer.

9 W.A. Herrmann, F.E. Kühn, M.U. Rauch, J.D.G. Correia and G. Artus, unpublished.

10 W.A. Herrmann, F.E. Kühn, C.C. Romão, M. Kleine and J. Mink, Chem. Ber., 127 (1994) 47.

11 (a) J.G. Kuchler, Ph.D. Thesis, Technische Universität München 1990; (b) W.A. Herrmann, F.E. Kühn, R.W. Fischer, W.R. Thiel and C.C. Romão, Inorg. Chem., 31 (1992) 4431; (c) W.A. Herrmann, F.E. Kühn and P.W. Roesky, J. Organomet. Chem., in press.

12 F.E. Kühn, W.A. Herrmann, R. Hahn, M. Elison, J. Blümel and E. Herdtweck, Organometallics, 13 (1994) 1601.

13 (a) J.W. Johnson, J.F. Brody, G.B. Ansell and S. Zentz, Inorg. Chem., 23 (1984) 2415; (b) W.A. Herrman, P.W. Roesky, M. Wang and W. Scherer, Organometallics, in press.