Journal of Organometallic Chemistry, 275 (1984) 153–160
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE CRYSTAL STRUCTURE OF A BIS-CARBENE COMPLEX OF GOLD(I), $\{[(trans,trans\text{-}p\text{-}CH_3C_6H_4NH)_2C]_2Au\}BF_4$

GUIDO BANDITELLI,
Centro CNR, Dipartimento di Chimica Generale ed Inorganica, via Venezian 21, I-20133 Milano (Italy)

FLAVIO BONATI,
Dipartimento di Scienze Chimiche dell'Università, I-62032 Camèrino (Italy)

SANDRO CALOGERO,
ICTR-CNR, Corso Stati Uniti 4, I-35100 Padova (Italy)

and GIOVANNI VALLE
Centro di Ricerche sui Biopolimeri del CNR, via Marzolo, I-35100 Padova (Italy)

(Received April 30th, 1984)

Summary

In the compound $[(Ar(H)N\overset{\cdots}{-}C\overset{\cdots}{-}N(H)Ar)_2Au]BF_4$ (Ar = *p*-tolyl) the two Au–C bonds (2.02(1) Å) are colinear (177.4(1)°). Both the HN hydrogens lie on the same side of the carbene ligands, on the side away from the gold atom, so that the two carbene ligands are in an unusual *trans,trans*-configuration.

Introduction

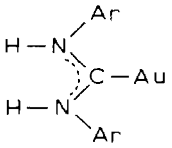
We recently began an investigation on gold complexes using Mössbauer spectroscopy [1], the parameters of which reveal fine electronic and structural details [2]. In particular, we have been investigating organogold derivatives such as substituted carbenes, e.g. $\{(RNH)(Q)C\}_2Au^+$, (RNH)(Q)CAuCl, or $\{(RNH)(Q)C\}_2AuX_2{}^+$ (Q = RNH or EtO; X = halogen), on which there have been extensive explorative studies [3].

In order to try and rationalize the Mössbauer data for such compounds an exact knowledge is required of the solid state structures. Although a reasonable structure has been proposed, mainly on the basis of analytical and spectroscopic data [4], an X-ray crystal structure is necessary in order, first, to ascertain that the structure in the solid state is the same as that established through solution data, such as NMR spectra or molecular weight determinations. If this is the case, a quantitative

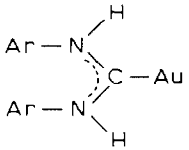
0022-328X/84/$03.00

measure of bond lengths and angles is obtained which gives an indication of the contributions of the possible canonical structures and which can support conclusions drawn from spectroscopic data alone. Secondly, the results of the structure determination not only confirm the nature of the coordination around the gold atom but can reveal such fine details as intermolecular interactions (e.g. Au...Au or hydrogen bonding), any deviation from linearity expected for two-coordinate species, the role of solvent molecules included in the crystals (clathrated or bonded in some way), and, finally, the reciprocal orientation of the ligands, which must be known in order to establish the nature of the gold–ligand bond(s).

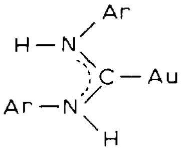
This paper presents the first X-ray crystal structure for a disubstituted carbene complex of gold(I) for which Mössbauer data are also available. The compound, $[\{(p\text{-tolyl})_2C\}_2Au]BF_4$, may adopt any of the three following stereoisomeric forms:



trans,trans



cis,cis



trans,cis

No such isomerisation is possible for the related alkyl(dialkylamino)carbene derivatives such as $ClAuC(Ph)(NMe_2)$ [5,6]. In the case of the complex we have studied, two isomers were detected by proton NMR, but only the more abundant was isolated, and for this the ^1H [1] and ^{13}C NMR spectra rule out a *trans,cis*-structure but do not allow a choice between the remaining two. The X-ray crystal structure determination has now shown that the two ligands are in the *trans,trans*-arrangement, and throws light on the role of ligand orientation and of hydrogen bonding in stabilizing this isomer.

Experimental

Preparation of the complex. A solution of $[(p\text{-MeC}_6H_4NC)_2Au]^+\ BF_4^-$ (1.98 g; 3.82 mmol) and *p*-toluidine (0.860 g; 8.03 mmol) in $CHCl_3$ (100 ml) was stirred at room temperature for 13 h. The colourless solution was evaporated to dryness, and the oily residue was stirred with n-hexane (ca. 70 ml) for 4 h. The crude solid (2.49 g) was recrystallized three times by slow addition of diethyl ether (ca. 100 ml) to its solution in dichloromethane (ca. 80 ml), to give an analytical sample (1.71 g; 68.6% yield). Elemental analysis: found: C, 49.43; H, 4.52; N, 7.65. $C_{30}H_{32}N_4AuBF_4$ calcd.: C, 49.19; H, 4.37; N, 7.65%. ^{13}C NMR spectrum ($CDCl_3$): 20.9 (*p*-Me), 123.0 and 129.4 (*ortho* and *meta*), 136.1 and 137.6 (*ipso* and *para*), 203.0 (carbene C) ppm from Me_4Si. ^1H NMR spectrum ($CDCl_3$): 7.67 s (*p*-Me), 6.84–7.20 pseudo-quartet (C_6H_4), 9.30 s (NH)(τ units).

Molecular weight determinations by osmometry (% w/w given): (a) 2127 (0.72), 2783 (1.32) in chloroform, indicating intramolecular hydrogen bonding, and (b) 555 (1.90), 488 (0.82) in acetone, corresponding to electrolyte dissociation; the formula weight is 731.8.

The crystals for the X-ray structure determination were obtained by slow evaporation (3 days) of the $CDCl_3$ solution employed for the NMR spectra.

The crystals belong to the monoclinic system with a 14.506(6) b 20.753(9), c 10.344(5) Å, β 105.7(3)°, $Z = 4$; U 2.997.8 Å^3, D_c 1.62 g cm^{-3}, $F(000)$ 1.440, space group $P2_1/n$. Intensity data were collected on a Phillips PW 1100 four-circle diffractometer in the range $4 < 2\theta < 50°$, Mo-K_α radiation. Using the criterion $I > 3\sigma(I)$, 2297 of the 5270 recorded independent intensities were considered observable. Lorentz and polarization corrections were applied. The structure was solved by a three-dimensional Patterson–Fourier synthesis from which the position of the gold atom was deduced. The other non-hydrogen atoms were located in a successive Fourier map.

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$). Esd's IN PARENTHESES

Atom	x/a	y/b	z/c
Au	7877(1)	9110(1)	7670(1)
N(1)	7189(12)	8333(7)	5162(16)
N(2)	8142(12)	7767(7)	6862(15)
N(3)	8526(11)	10397(7)	8879(14)
N(4)	7672(11)	9844(7)	10029(14)
C(1)	7712(12)	8344(9)	6422(21)
C(2)	8020(11)	9851(8)	8979(17)
C(3)	6603(8)	8870(5)	4560(13)
C(4)	5610(8)	8798(5)	4160(13)
C(5)	5029(8)	9319(5)	3609(13)
C(6)	5441(8)	9912(5)	3458(13)
C(7)	6434(8)	9984(5)	3858(13)
C(8)	7015(8)	9463(5)	4409(13)
C(9)	4806(23)	10495(14)	2922(28)
C(10)	8918(9)	10527(7)	7771(11)
C(11)	8324(9)	10663(7)	6497(11)
C(12)	8722(9)	10827(7)	5455(11)
C(13)	9715(9)	10855(7)	5688(11)
C(14)	10309(9)	10719(7)	6963(11)
C(15)	9911(9)	10555(7)	8005(11)
C(16)	10136(17)	11013(11)	4557(23)
C(17)	8661(8)	7653(6)	8224(9)
C(18)	9497(8)	8000(6)	8792(9)
C(19)	9982(8)	7912(6)	10142(9)
C(20)	9632(8)	7477(6)	10923(9)
C(21)	8797(8)	7131(6)	10355(9)
C(22)	8311(8)	7219(6)	9006(9)
C(23)	10205(20)	7372(15)	12360(28)
C(24)	7110(8)	9338(5)	10341(12)
C(25)	6204(8)	9473(5)	10498(12)
C(26)	5634(8)	8975(5)	10760(12)
C(27)	5970(8)	8342(5)	10865(12)
C(28)	6876(8)	8207(5)	10708(12)
C(29)	7446(8)	8705(5)	10446(12)
C(30)	5344(25)	7799(15)	11113(32)
B	2610(19)	3460(14)	6037(28)
F(1)	2698(16)	2880(12)	6322(22)
F(2)	2195(17)	3477(12)	4594(26)
F(3)	1919(21)	3807(13)	6340(28)
F(4)	3407(11)	3843(7)	6263(15)

A full-matrix least-squares refinement of F was computed, by minimizing the function $\Sigma w(|F_0|-|F_c|)^2$ where $w = 2.3817/(\sigma^2(F)+0.001521F^2)$. The SHELX programs were used [7]. Only the atoms in the coordinate sphere of the gold together with the nitrogen atoms were refined anisotropically. The phenyl carbon atoms were refined as a rigid body. The position of the hydrogen atoms were located but not refined. The final R value is 0.0683, with $R_w = 0.0697$. The final atomic coordinates are listed in Table 1, and the bond distances and angles in Table 2. A list of the structure factors, thermal parameters, and least-squares planes can be obtained from the authors on request.

Results and discussion

The stereochemical arrangement in the compound is shown in Fig. 1 together with the atom-numbering scheme. The geometry of the BF_4^- anion is only roughly

TABLE 2

BOND DISTANCES (Å) AND BOND ANGLES (°) WITH esd's IN PARENTHESES

$[(CH_3C_6H_4NH)_2C]_2Au^+$			
Au–C(1)	2.02(2)	C(1)–Au–C(2)	177.4(7)
Au–C(2)	2.02(2)	Au–C(1)–N(1)	126(1)
C(1)–N(1)	1.32(2)	Au–C(1)–N(2)	121(1)
C(1)–N(2)	1.37(2)	N(1)–C(1)–N(2)	114(2)
C(2)–N(3)	1.37(2)	Au–C(2)–N(3)	123(1)
C(2)–N(4)	1.32(2)	Au–C(2)–N(4)	123(1)
N(1)–C(3)	1.44(2)	N(3)–C(2)–N(4)	114(1)
N(2)–C(17)	1.43(2)	C(1)–N(1)–C(3)	122(1)
N(3)–C(10)	1.44(2)	C(1)–N(2)–C(17)	123(1)
N(4)–C(24)	1.42(2)	C(2)–N(3)–C(10)	124(1)
C(6)–C(9)	1.53(3)	C(2)–N(4)–C(24)	125(1)
C(13)–C(16)	1.50(2)	N(1)–C(3)–C(4)	119(1)
C(20)–C(23)	1.51(3)	N(1)–C(3)–C(8)	121(1)
C(27)–C(30)	1.51(3)	N(2)–C(17)–C(18)	120(1)
		N(2)–C(17)–C(22)	120(1)
		N(3)–C(10)–C(11)	121(1)
		N(3)–C(10)–C(15)	119(1)
		N(4)–C(24)–C(25)	120(1)
		N(4)–C(24)–C(29)	120(1)
		C(5)–C(6)–C(9)	120(1)
		C(7)–C(6)–C(9)	120(1)
		C(12)–C(13)–C(16)	120(1)
		C(14)–C(13)–C(16)	120(1)
		C(19)–C(20)–C(23)	118(1)
		C(21)–C(20)–C(23)	122(1)
		C(26)–C(27)–C(30)	120(1)
		C(28)–C(27)–C(30)	120(1)
BF_4^-			
B–F(1)	1.24(3)	F(1)–B–F(2)	105(2)
B–F(2)	1.45(3)	F(1)–B–F(3)	120(3)
B–F(3)	1.34(3)	F(1)–B–F(4)	120(3)
B–F(4)	1.37(3)	F(2)–B–F(3)	96(2)
		F(2)–B–F(4)	105(2)
		F(3)–B–F(4)	107(2)

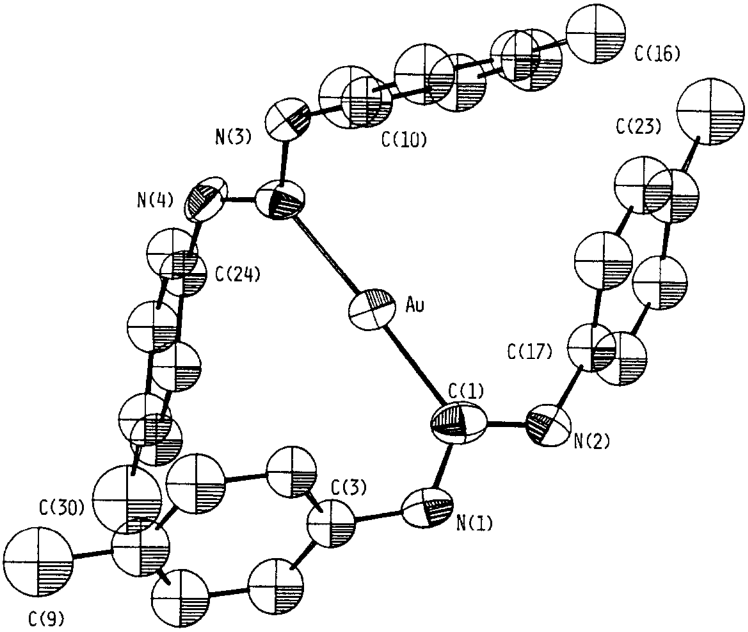


Fig. 1. The stereochemical arrangement of the $[\{(p\text{-}CH_3C_6H_4NH)_2C\}_2Au]^+$ cation

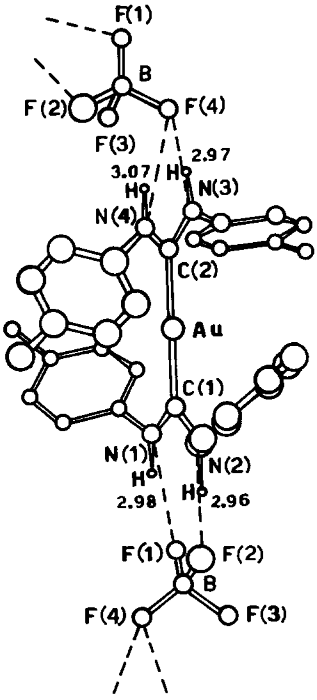


Fig. 2. A perspective view of $[\{(p\text{-}CH_3C_6H_4NH)_2C\}_2Au]BF_4$.

TABLE 3

INTERATOMIC DISTANCES LESS THAN 3.5 Å.

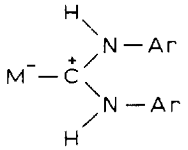
N(1)...F(1) [a]	2.98 I	N(3)...F(4) [a]	2.97 II
N(2)...F(1)	3.46	N(4)...F(2)	3.56
N(2)...F(2) [a]	2.96 I	N(4)...F(3)	3.41
N(3)...F(2)	3.24	N(4)...F(4) [a]	3.07 II

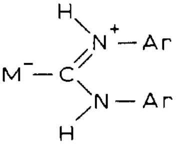
[a] Possible hydrogen bond. Symmetry Operators: (I) $1-x, 1-y, 1-z$; (II) $-\frac{1}{2}+x, \frac{3}{2}-y, -1/2+z$.

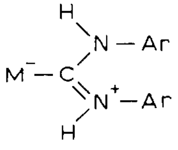
tetrahedral owing to the hydrogen bonds listed in Table 3 and shown in Fig. 2. The N(1) and N(2) atoms are connected to the F(1) and F(2) of BF_4^-, while N(3) and N(4) are connected to the F(4) atom of a different BF_4^- anion. The unconnected F(3) thus shows the largest positional disorder and thermal effect. The network of NH...F hydrogen bonds, as shown in Fig. 2, tends to give rise to a linear polymer in the solid state, so providing a possible explanation of the results of molecular weight determinations by osmometry in chloroform: the values found are generally higher than the formula weight for this and for several other, related compounds [4].

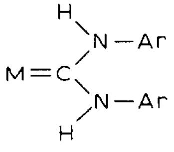
Within the cation the gold atom is linearly coordinated, with a C–Au–C angle of 177.4(7)°. This is consistent with the Mössbauer parameters (isomer shift 4.45, quadrupole splitting 10.73 mm/sec), which are typical of two-coordinate gold(I). The presence of a Mössbauer quadrupole-split doublet with a linewidth of about 2.01 mm/sec, close to the minimum observable width for ^{197}Au, is consistent with the presence of only one gold site in the compound and with the absence of any Au...Au interaction less than 4.8 Å.

In each ligand the two nitrogen atoms, the carbene carbon, and the gold atoms lie in a plane, and the two planes make a dihedral angle of 68.1°; the phenyl rings are folded, as can be seen by inspection of the values of the angles given in Table 4. In each ligand the carbene atom is sp^2-hybridized; the angles around it are in the range 114–126 or 114–123°, and the $\mathrm{C \overset{\cdots}{-} N}$ distances (1.32–1.37(2) Å) are intermediate between the values observed for a single (1.47 Å) and a double bond (1.255(12) Å in $Ph_3PAuC(OMe){=}NC_6H_4$-*p*-Me [8]). The lower limit is approached in the case of $ClAuC(Ph)(NMe_2)$ [6], for which $\mathrm{C \overset{\cdots}{-} N}$ is 1.27(4) Å and the NCC_{phenyl} angle is 118(3)°. In the closely related gold(III) derivative $[trans\text{-}\{(ArNH)_2C\}_2AuI_2]^+$ the angles range from 112(1) to 127(1)°, and the $\mathrm{C \overset{\cdots}{-} N}$ distances from 1.27(3) to 1.35(2) [9]. Clearly in both of the disubstituted carbene derivatives the contribution of the canonical forms **b** and **c** is significant, as shown independently by the intensity of the infrared vibration at ca. 1545 cm^{-1}, and by the existence of stable isomers in solution (^{1}H and ^{13}C NMR evidence).


(a)


(b)


(c)


(d)

The gold–carbon distance in linear gold(I) complexes is very sensitive to the ligand *trans* to it, as it can be seen in the series LAuCN where L is CN (2.12 Å [10]),

TABLE 4

INDIVIDUAL DEVIATIONS, IN Å, OF SIGNIFICANT ATOMS FROM ORTHOGONALIZED LEAST-SQUARES PLANES

Plane number	Atoms defining the plane	Bihedral angles (deg)					
I	Au,N(1),N(2),C(1)	I–II	68.1	II–III	78.7	IV–V	35.1
II	Au,N(3),N(4),C(2)	I–III	117.8	II–IV	108.7	IV–VI	69.8
III	C(3),C(4),C(5),C(6),C(7),C(8),C(9)	I–IV	82.3	II–V	127.2	V–VI	74.6
IV	C(10),C(11),C(12),C(13),C(14),C(15),C(16)	I–V	116.5	II–VI	53.3		
V	C(17),C(18),C(19),C(20),C(21),C(22),C(23)	I–VI	97.4	III–IV	60.3		
VI	C(24),C(25),C(26),C(27),C(28),C(29),C(30)			III–V	51.6		
				III–VI	26.5		

	Plane I	Plane II	Plane III	Plane IV	Plane V	Plane VI
Au	−0.0022	0.0040	2.6992	−2.7607	2.6614	−2.4298
N(1)	−0.0032	−0.9421	0.0745	−4.9015	1.0093	−5.1218
N(2)	−0.0029	1.1443	1.0565	−5.6986	0.0317	−3.4777
N(3)	0.9571	0.0054	4.3179	0.0667	4.5463	−0.8400
N(4)	−1.1283	0.0057	5.5372	−0.6444	5.0006	−0.0636
C(1)	0.0083	0.0437	1.1128	−4.6075	1.1034	−3.8304
C(2)	−0.0899	−0.0151	4.3426	−0.9456	4.2287	−0.9824
C(3)	−0.1338	−2.2286	0.0149	−3.9156	2.0918	−5.6676
C(10)	2.1583	−0.0962	3.1125	−0.0079	3.8945	−1.7738
C(17)	−0.1262	2.2700	2.1312	−5.6282	−0.0144	−2.1226
C(24)	−2.3419	−0.0314	5.8192	−1.5144	4.8383	−0.0073

or Me–NC (2.01(4) Å [11]), or Ph_3P (1.85(4) Å [12]): unfortunately the results available are not abundant and, sometimes, poorly accurate. The Au–C bond in our compound (2.02(1) Å) is equal to that in $ClAuC(Ph)(NMe_2)$(2.03(3) Å [6]), and to those reported for another Au–C(sp^2) bond *trans* to Ph_3P (L′), i.e. 2.012–2.056(16) in $L'AuC(OEt){=}NC_6H_4$-*p*-Me [8]; it is longer than in $[AuC(OEt){=}NC_6H_4$-*p*-$Me]_3$ (1.935–1.975(20)Å [13]), in which, however, Au...Au interactions are present. Finally, the Au–C distance is comparable with those found in various complexes containing the L′Au–C(sp^2) moiety: 2.07(2) Å in $L'AuC_6F_5$ [14], or 2.05(6) Å in $L'Au{-}C(CF_3){=}C(CF_3)AuL'$ [15]. On this evidence it can be assumed that the contribution of a form containing a Au–C bond with a bond order higher than unity (formula **d**) is small (if there is any), in agreement with the Mössbauer data which suggests the absence of a significant π-interaction. Furthermore, the value of the Au–C distance also indicates that the *trans*-influence of the $(aryl\text{-}NH)_2C$ ligand is comparable with that of a triarylphosphine, in agreement with Au–Cl stretching frequency in LAuCl compounds at 324 to 329 cm^{-1} when L is $(aryl\text{-}NH)_2C$ or Ph_3P, respectively [16]. Similarly, structural considerations suggest that in the above mentioned gold(III) derivative the carbene ligands exert a considerable *trans*-influence [9].

In our compound the aryl substituents on the N$\overset{...}{-}$C$\overset{...}{-}$N moiety are in the *trans,trans*-configuration, which seems less favoured than a *trans,cis*-configuration because of steric hindrance. The latter type of configuration was established by an X-ray crystal structure determination for a related gold(III) derivative, namely [*trans*-$\{(ArNH)_2C\}_2AuI_2]^+$ [9]. The *trans,trans*-configuration is probably favoured in our compound because the dihedral angle of 68.1° between the carbene planes, and the folding of the phenyl rings accommodate the steric requirements of the ligands, which are then fixed in their positions by NH... F hydrogen bondings to the anion.

Acknowledgements

Partial support by the "Consiglio Nazionale delle Ricerche-Comitato Tecnologico", Rome, and by the Ministry of "Pubblica Istruzione" is acknowledged.

References

1 G. Banditelli, F. Bonati, S. Calogero and F.E. Wagner, unpublished results
2 R.J. Puddephatt, The Chemistry of Gold, Elsevier Amsterdam, 1978, p.226–234; R.V. Parish and J.D. Dush, Chem. Phys. Letters, 63 (1979) 37; R.V. Parish, O. Parry and C.A. McAuliffe, J. Chem. Soc. Dalton Trans., (1981) 2095; R.V. Parish in P. Guetlich and G.M. Kalvius (Eds.), Trends in Moessbauer Spectroscopy, Second Seeheim Workshop, 1983, p. 56.
3 H. Schmidbaur, Organogold Compounds, Gmelin Handbuch der Anorganischen Chemie, Springer-Verlag, Berlin 1980, pp.169–189.
4 G. Minghetti, L. Baratto and F. Bonati, J. Organomet. Chem., 102 (1975) 397.
5 E.O. Fischer, M. Bock and R. Aumann, Chem. Ber., 116 (1983) 3618.
6 U. Schubert, K. Ackermann and R. Aumann, Cryst. Struct. Commun., 11 (1982) 591; R. Aumann and E.O. Fischer, Chem. Ber., 114 (1981) 1853.
7 G. Sheldrick, SHELX 76 System of Computing Programs, University of Cambridge, 1976
8 M. Lanfranchi, M.A. Pellinghelli, A. Tiripicchio and F. Bonati, Acta Crystallogr., submitted.
9 L. Manojlović-Muir, J. Organomet. Chem., 73 (1974) C45.
10 A Rosenzweig and D.T Cromer, Acta Crystallogr , 12 (1959) 709.
11 S Esperas, Acta Chem Scandinav., A30 (1976) 527
12 P.L. Bellon, M. Manassero and M Sansoni, Ric Sci , 39 (1969) 173
13 A. Tiripicchio, M T. Camellini and G Minghetti, J. Organomet. Chem., 171 (1979) 399
14 R.W. Baker and P.J. Pauling, J Chem. Soc. Dalton Trans , (1972) 2264.
15 C.J. Gilmore and P Woodward, J. Chem. Soc Chem Comm., (1971) 1233
16 F. Bonati and G. Minghetti, Gazz Chim Ital., 103 (1973) 373