Contribution from the CNR Center, Istituto di Chimica Generale dell'Università, 20133 Milano, Italy,
and from the Istituto Chimico dell'Università, 62032 Camerino, Italy

Bis[(methoxy)(*N*-arylimino)methyl]platinum(II) Derivatives. A New Type of Ligand[1a]

GIOVANNI MINGHETTI,[1b] FLAVIO BONATI,*[1c] and GUIDO BANDITELLI[1b]

Received July 30, 1975 AIC50563D

The compounds $(Ph_2PCH_2)_2Pt[C(OMe)({=}NAr)]_2$ (L) or $(Ph_3P)(ArNC)Pt[C(OMe)({=}NAr)]_2$ (L′) (Ar = 4-tolyl) are bifunctional bases and potentially bidentate nitrogen ligands. Indeed, they react with picric or fluoboric acid yielding LH_2^{2+} or $L'H_2^{2+}$; they also react with $CdBr_2$, CdI_2, $HgCl_2$, $AgBF_4$, and $[Rh(CO)_2Cl]_2$ affording 1:1 adducts, where two (or more) different metal atoms are connected by unsaturated bridging $-C(OMe){=}N(Ar)$ groups. In some cases (Cd, Co, Hg), compound L acts as a chelating ligand and bimetallocycles are formed.

Introduction

A new class of stable σ-bonded organic derivatives of metals is now available through the reaction patterns (1), (2a), and (3) which lead to the same type of (alkoxy)(*N*-alkylamino)methylmetal compound, A, where M indicates a metal (silver,[2] gold,[3,4] mercury,[2] platinum,[4b,5,6] palladium[7]) with or without suitable attached ligands.

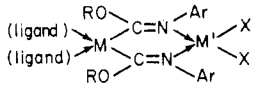
$$R{-}NC + M^{n+} + nOH^- + R'OH \xrightarrow{-H_2O} \qquad (1)$$

$$(R{-}NH)(R'O)C{\rightarrow}M^{n+} \underset{(b)\ +H^+}{\overset{(a)\ +OH^-}{\rightleftarrows}} \underset{\mathrm{A}}{(R{-}N{=})(R'O)C{-}M} \qquad (2)$$

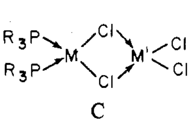
$$[(R{-}N{=})(R'O)C{-}Ag]_3 + 3MX \xrightarrow{-3AgX} \qquad (3)$$

It is known that the nitrogen of these complexes may be protonated to afford carbene complexes according to reaction 2b; for example in the case of $(Ph_3P)AuC(OMe)({=}NAr)$ or of $Hg[C(OEt){=}NAr]_2$ a mono- and a dipicrate, respectively, were isolated.[8] By extension, the reaction with suitable acceptors was carried out and it was found[8] that these molecules can act as either monodentate or bidentate nitrogen ligands, affording complexes like $[\{(Ph_3P)AuC(OMe){=}NAr\}_2Ag^+]ClO_4^-$ and $\{(CO)_2ClRh[ArN{=}C(OEt)]\}_2Hg$.

It was therefore of interest to look for bidentate but chelating ligands of this new type, so that by reaction with a suitable acceptor, bimetallic complexes like B should be formed. In such complexes there is a bimetallocycle and the two metal atoms are not necessarily as electronically insulated as in the case of the complexes obtained from the other metal-containing ligands, such as C[9] or D,[10] but they are rather likely to influence each other in the same way as in compound E.[11]

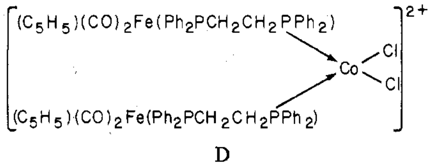


B

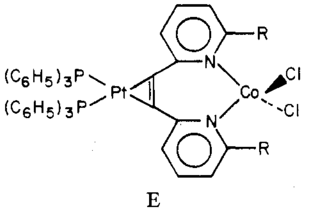


C

M = Pt; M′ = Hg
M = Hg; M′ = Co or Ni



D



E

The $[(RO)(R{-}N{=})C]_nM(\text{ligand})_m$ species can formally be considered as C-metalated homologues of alkyl formimidates, $(RO)(R{-}N{=})CH$. Just as these compounds may react with suitable acceptors to yield complexes,[12] which are rather unstable, so the C-metalated homologues may be ligands, even chelating ligands if they are bifunctional, affording the bimetallic complexes described below.

Experimental Section

Analyses were performed by the microanalytical laboratory of this department (Istituto di Chimica Generale dell'Università, Milano) and by Dr. Pascher's Mikroanalytisches Laboratorium, Bonn. The presence of the different metals in the bimetallic compounds was always checked at least by qualitative analysis. Infrared spectra were recorded on a Perkin-Elmer 457 instrument, NMR spectra on a Varian NEVA (60 Mc), and electronic spectra on a Beckman DK2; the conductivity measurement was done on a Philips conductance bridge, and molecular weight measurement (osmometry) on a Mechrolab osmometer.

Throughout this paper L is $(Ph_2PCH_2CH_2PPh_2)Pt[C(OMe){=}NAr]_2$ and L′ is $(Ph_3P)(ArNC)Pt[C(OMe){=}NAr]_2$, whose Ar is 4-tolyl.

Evaporation was always carried out under reduced pressure (water aspirator). Analytical and other data are shown in Table I and NMR data in the Table II.

[1,2-Bis(diphenylphosphino)ethane]bis[(methoxy)(*N*-*p*-tolylimino)methyl]platinum(II), L, I. To a stirred methanol (20 ml) suspension of $(Ph_2PCH_2)_2PtCl_2$ (250 mg; 0.376 mmol) potassium hydroxide (48 mg; 0.86 mmol) in the same solvent (6 ml) and *p*-tolyl isocyanide (0.11 ml; 0.86 mmol) were added giving a white precipitate. After 0.5 h the precipitate was filtered and purified by dissolving it in dichloromethane; on concentration of the filtered solution an analytical sample (200 mg; 60%) of I was obtained, mp 244 °C, after some decomposition at ca. 218 °C.

$[LH_2^{2+}][C_6H_2(NO_2)_3O^-]_2$, II. To a stirred saturated solution of I (200 mg; 0.225 mmol) in diethyl ether (800 ml) picric acid (110 mg; 0.48 mmol) (*warning*! explosive) in the same solvent (110 ml) was added. After 20 min the solution was concentrated to ca. 30 ml, and the yellow precipitate was filtered and washed repeatedly with ether to afford the analytical sample, mp 115–117 °C; $\Lambda = 200\ \Omega^{-1}\ cm^2\ mol^{-1}$ (22 °C; 2×10^{-4} M acetone solution).

$[LH_2^{2+}][BF_4^-]_2$, III. To a stirred suspension of I (200 mg; 0.225 mmol) in methanol (50 ml) 50% aqueous fluoboric acid (0.65 ml; 5.0 mmol) was added. The clear solution was evaporated to dryness and the residue was crystallized from CH_2Cl_2/Et_2O (ca. 10:30 v/v) to yield the compound (210 mg; 88%); an additional crystallization gave the analytical sample, mp 148–149 °C, after some decomposition around 140 °C; $\Lambda = 222\ \Omega^{-1}\ cm^2\ mol^{-1}$ (19 °C; 2.5×10^{-4} M acetone solution).

$[LH_2^{2+}]_2[CoCl_4^{2-}][Cl^-]_2$, IV. To a stirred methanol (20 ml) suspension of I (200 mg; 0.225 mmol) a solution of $CoCl_2{\cdot}6H_2O$ (101 mg; 0.74 mmol) in the same solvent (20 ml) was added. After 1 h the filtered solution was evaporated to dryness. The solid residue was crystallized at room temperature twice from CH_2Cl_2/Et_2O (15:5 v/v) or, alternatively, from $MeOH/Et_2O$ to yield the blue analytical sample (150 mg; 59%), mp 168–170 °C (on being heated in the air, the compound became green at ca. 150 °C, the exact temperature depending on the rate of heating). At 22 °C a 1.3×10^{-4} M

Table I. Analytical[a] and Other Data

No.	Compd,[b] color	Mol wt[a]	% C	% H	% N	Ir data[c]
I	L, white	770 (C_6H_6) (889)	59.4 (59.40)	4.80 (4.95)	3.04 (3.15)	ν(C=N) 1575
II	$[LH_2^{2+}][C_6H_2(NO_2)_3O^-]_2$, yellow	(1347)	50.18 (49.90)	3.81 (3.71)	8.00 (8.31)	See text
III	$[LH_2^{2+}][BF_4^-]_2$, white	(1065)	49.60 (49.58)	4.32 (4.32)	2.46 (2.63)	ν(N–H) 3600, 3500, 3210 m, ν(C=N) 1545, ν(B–F) 1070 vs
IV	$[LH_2^{2+}][CoCl_4^{2-}][Cl^-]_2$,[d] blue	(2054)	51.25 (51.41)	4.54 (4.48)	2.74 (2.73)	ν(N–H) 3400 w, ν(C=N) 1555, ν(Co–Cl) 290
V	$L\cdot HgCl_2$, white	(1161)	45.10 (45.48)	3.81 (3.79)	2.47 (2.41)	ν(C=N) 1530, ν(Hg–Cl) 265
VI	$L\cdot 2[(CO)_2RhCl]$, yellow	(1278)	45.53 (45.07)	3.43 (3.45)	2.28 (2.19)	ν(CO) 2050, 1967, ν(C=N) 1510, ν(Rh–Cl) 310 m, b
VII	$L\cdot CoCl_2$,[e] blue	900 ($CHCl_3$) (1019)	51.74 (51.82)	4.40 (4.32)	2.71 (2.75)	ν(C=N) 1530, ν(Co–Cl) 304
VIII	$L\cdot CdBr_2$,[f] white	1141 (CH_2Cl_2) (1161)	45.87 (45.48)	3.68 (3.79)	2.41 (2.41)	ν(C=N) 1530, 1543 in CH_2Cl_2
IX	$L\cdot CdI_2$,[g] white	1164 (CH_2Cl_2) (1255)	42.83 (42.07)	3.48 (3.51)	2.28 (2.23)	ν(C=N) 1528
X	L′, white	(870)	61.09 (60.70)	4.09 (4.82)	4.73 (4.82)	ν(C≡N) 2175, ν(C=N) 1573
XI	$[L'H_2^{2+}][BF_4^-]_2$, white	(1046)	50.50 (50.48)	4.20 (4.21)	4.02 (4.02)	ν(C≡N) 2205, ν(N–H) 3210, δ(N–H) 1600, ν(C=N) 1545
XII	$L'\cdot AgBF_4$, white	(1065)	49.32 (49.58)	4.30 (3.94)	3.80 (3.94)	ν(C≡N) 2190, ν(C=N) 1525, ν(B–F) 1050 vs, b
XIIIa	$L'\cdot HgCl_2$, white	1064 ($CHCl_3$) (1142)	46.65 (46.23)	3.86 (3.68)	3.52 (3.68)	ν(C≡N) 2210, ν(C=N) 1580, 1540
XIIIb	$L'\cdot HgCl_2\cdot CHCl_3$,[h] white	(1261)	43.34 (42.82)	3.49 (3.41)	3.51 (3.33)	ν(C≡N) 2200, ν(C=N) 1575, 1540, ν(Hg–Cl) 275
XIV	$L'\cdot 2[(CO)_2RhCl]$, pale yellow	(1259)	45.65 (45.75)	3.20 (3.34)	3.30 (3.34)	ν(C≡N) 2200, ν(CO) 2065, 1990, ν(C=N) 1550, 1530, ν(Rh–Cl) 310

[a] Calculated values in parentheses. [b] L = $(Ph_2PCH_2)_2Pt[C(OCH_3)=NC_6H_4CH_3\text{-}p]_2$; L′ = $(Ph_3P)(p\text{-}CH_3C_6H_4NC)Pt[C(OCH_3)=NC_6H_4CH_3\text{-}p]_2$. [c] Nujol mull. [d] Percent values: Pt, 19.25 (18.99); Co, 2.46 (2.87); Cl, 10.06 (10.37). [e] Percent values: Co, 6.32 (5.79); Cl, 7.78 (6.97). [f] Percent values: Cd, 9.52 (9.68); Br, 14.32 (13.75). [g] Percent values: Cd, 9.26 (8.96); I, 20.45 (20.23). [h] In a different preparation a compound was obtained which analyzed as 44.35% C, 3.47% H, 3.61% N; $L'\cdot HgCl_2\cdot 0.5CHCl_3$ requires 44.43% C, 3.54% H, and 3.49% N.

acetonitrile solution gave $\Lambda = 242\ \Omega^{-1}\ cm^2\ mol^{-1}$ at 18 °C and a 3.2×10^{-4} M nitromethane solution gave $\Lambda = 187\ \Omega^{-1}\ cm^2\ mol^{-1}$. According to Evans' method,[12] the magnetic moment, corrected for diamagnetism, was found to be 4.3 μ_B at 40 °C in chloroform solution. Electronic spectrum: in $CHCl_3$, λ_{max} 701 nm (ϵ 526), 677 nm (ϵ 502), 643 nm (ϵ 365). Reflectance spectrum: λ_{max} 672, 637 nm.

$L\cdot HgCl_2$, V. The ligand I (150 mg; 0.17 mmol), diethyl ether (30 ml), and an ethereal solution (10 ml) of mercury(II) chloride (92 mg; 0.34 mmol) were stirred for 2 h. The white precipitate was filtered and washed with diethyl ether, to afford the analytical sample, mp 148 °C dec. The compound is not sufficiently stable in solution for NMR or conductance measurement. The compound reacted immediately with an acetone solution containing α,α'-dipyridyl (1:1 ratio); the white precipitate was filtered and identified as (α,α'-bpy)$HgCl_2$, while the residue left after evaporation of the mother liquor was identified as the ligand I (melting point and ir spectrum).

$L\cdot[(CO)_2RhCl]_2$, VI. A diethyl ether solution (10 ml) of tetracarbonyl-μ-dichloro-dirhodium(I) (66 mg; 0.256 mmol) was added to a stirred ethereal (30 ml) suspension of the ligand I (150 mg; 0.17 mmol). After stirring of the mixture for 2 h, the yellow precipitate was filtered and washed with ether to yield the product (120 mg; 55% on platinum), mp 163 °C dec. In solution the compound is not sufficiently stable to allow measurements to be carried out.

The solid yellow compound reacted at once with an ethereal solution of triphenylphosphine in a 1:4 ratio. The yellow solid which formed was identified (ir spectrum and melting point) as *cis*-$(Ph_3P)_2Rh(CO)Cl$; the mother liquor was evaporated to dryness; the residue was dissolved in benzene, and a white precipitate was obtained by concentration of the solution to which methanol had been added and was identified as the ligand I (ir spectrum and melting point).

$L\cdot CoCl_2$, VII. The reaction was carried out in anhydrous conditions and under nitrogen. A stirred mixture of anhydrous cobalt(II) chloride (34 mg; 0.26 mmol) and of the ligand L (294 mg; 0.33 mmol) in diethyl ether (40 ml) was refluxed for 3 days. On filtration of the suspension at room temperature, the crude product was obtained (230 mg) and was purified by adding pentane to the chloroform solution (30 ml) to yield the analytical sample, stable in air up to ca. 165 °C, at which temperature it became green; $\Lambda = 3.6\ \Omega^{-1}\ cm^2\ mol^{-1}$ (25 °C, 0.88×10^{-3} M in CH_2Cl_2). According to Evans' method, the compound is paramagnetic in $CHCl_3$ solution (3.1 μ_B). Electronic spectra: in chloroform solution, λ_{max} 668 nm (ϵ 258), 638 nm (ϵ 299), 600 nm (ϵ 244); in the solid state, λ_{max} 627, 597 (sh) nm.

$L\cdot CdBr_2$, VIII. Compound I (190 mg; 0.214 mmol), $CdBr_2\cdot 4H_2O$ (36 mg; 0.10 mmol), and diethyl ether were stirred for 2 days. The white product (170 mg) was filtered and purified from CH_2Cl_2/Et_2O (5:40 v/v) to yield the analytical sample (130 mg), dec pt ca. 150 °C, soluble in CH_2Cl_2 and sparingly soluble in $CHCl_3$.

$L\cdot CdI_2$, IX. This was prepared and purified in a manner analogous to that for VIII. The white compound is soluble in CH_2Cl_2, where it is a nonelectrolyte.

(Triphenylphosphine)(*p*-tolyl isocyanide)bis[(methoxy)(*N*-*p*-tolylimino)methyl]platinum(II), L′, X. This was obtained according to a literature procedure.[5]

$[L'H_2^{2+}][BF_4^-]_2$, XI. Aqueous fluoboric acid (1.6 ml of a 50% solution; 12.4 mmol) was added to a stirred methanol (100 ml) solution of the ligand X (435 mg; 0.50 mmol). After concentration of the mixture to dryness, the wet residue was extracted with chloroform (50 ml), the aqueous layer was removed, and the organic phase was dried over Na_2SO_4. The solution was again evaporated to dryness, and the residue was washed with petroleum ether and crystallized from CH_2Cl_2/Et_2O (ca. 10:40 v/v) to yield the crude product (380 mg), which was crystallized again to afford the analytical sample (250 mg), mp 188 °C with a change to yellow color at ca. 120 °C. In a 2.7×10^{-4} M acetone solution Λ was found to be 198 $\Omega^{-1}\ cm^2\ mol^{-1}$ at 15 °C.

$L'\cdot AgBF_4$, XII. Silver tetrafluoroborate (142.6 mg; 0.73 mmol) was added to a benzene solution (30 ml) of the ligand X (320 mg; 0.368 mmol). After stirring of the mixture for 1 h, the white, light-sensitive precipitate (320 mg) was filtered; it was purified by crystallization from CH_2Cl_2/petroleum ether, affording the analytical sample (240 mg), mp 147 °C, dec pt ca. 120 °C. At 15 °C a 5×10^{-4} M acetone solution had $\Lambda = 140\ \Omega^{-1}\ cm^2\ mol^{-1}$.

$L'\cdot HgCl_2$, XIIIa and XIIIb. Mercury(II) chloride (70 mg; 0.26 mmol) in diethyl ether (20 ml) was added to a stirred suspension of compound X (230 mg; 0.26 mmol) in the same solvent (20 ml). After 20 min the product was filtered (290 mg; 97%) and analyzed as XIIIa. Compound XIIIa could be crystallized from $CHCl_3/Et_2O$ (3:8 v/v) to yield the $CHCl_3$ adduct, XIIIb, mp 134 °C (nonelectrolyte in

Table II. ^{1}H NMR Data

Compd	Solvent	CH_2	*p*-CH_3	OCH_3	C_6H_4	C_6H_5	Other(s)
I	$CDCl_3$	8.5–7.75 m	7.64 s	6.80 s ^4J(Pt–H) ≃ 6 Hz	3.69, 3.60 3.10, 2.97	2.8–2.2 m	
I	C_6D_6	9–8 m	7.60 s	6.52 s ^4J(Pt–H) ≃ 6 Hz	3.5–2.3 m		
II	$CDCl_3$	8.15 b	7.64 s	6.22 s ^4J(Pt–H) ≃ 4 Hz	3.5–1.8 m 1.105 (picric acid)		−2.53 (NH)
III	CD_2Cl_2	7.5–6.25 m	7.69 s	5.99 s ^4J(Pt–H) ≃ 4 Hz	2.90	2.70–1.8 m	−0.35 b (NH)
VIII	CD_2Cl_2	*a*	7.76 s	6.17 s ^4J(Pt–H) ≃ 3.5 Hz	3.67, 3.53 3.15, 2.98	2.7–1.9 m	
IX	CD_2Cl_2	*a*	7.74 s	6.20 s ^4J(Pt–H) ≃ 3.8 Hz	3.60, 3.47 3.07, 2.93	2.7–1.9 m	
X	$CDCl_3$		7.76 s, 7.70 s, 7.65 s	6.39 s, 6.18 s ^4J(Pt–H) ≃ 6 Hz	3.75–2.50 m		
X	C_6D_6		8.32 s, 7.72 s	6.03 s, 5.83 s ^4J(Pt–H) ≃ 6 Hz	3.85–2.1 m		
XI	CD_2Cl_2		7.74 s, 7.72 s, 7.70 s	5.54 s, 5.22 s ^4J(Pt–H) ≃ 3.5 Hz	3.5–2.0 m		−0.21 s −0.96 s (NH)
XII	$CDCl_3$		7.84 s, 7.72 s, 7.59 s	6.34 s, 5.35 s	3.7–2.0		
XIIIb	$CDCl_3$		7.72 s, 7.67 s, 7.63 s	6.20 b	3.7–2.0 m		
XIV	$CDCl_3$		7.75 s, 7.69 s	7.19 s, 6.59 s, 6.15 s, 5.60 s ^4J(Pt–H) ≃ 3 Hz	3.9–2.0 m		

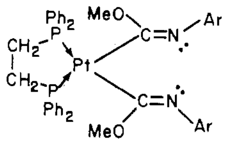
[a] CH_2 signals were not detected but integration revealed that they lie at ca. 7.5–8.5 ppm.

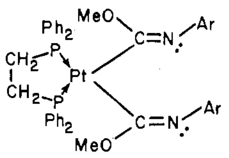
acetone). An additional ir band is found at 745 cm^{-1} and is assigned to chloroform.

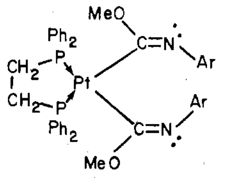
L′·2[(CO)$_2$RhCl], XIV. On addition of [(CO)$_2$RhCl]$_2$ (53.7 mg; 0.138 mmol) in the minimum amount of diethyl ether to a stirred suspension of the ligand X (120 mg; 0.138 mmol) in the same solvent a yellow precipitate formed at once. After 15 min, the crude compound (80 mg) was filtered, washed with ether, and crystallized from the minimum amount of CH_2Cl_2/Et_2O to yield the analytical sample (50 mg), mp 127 °C, dec pt ca. 120 °C (nonelectrolyte in acetone where it is not stable for long).

Results and Discussion

The compounds $(Ph_2PCH_2CH_2PPh_2)Pt[C(OMe){=}NAr]_2$ (I) and $(Ph_3P)(ArNC)Pt[C(OMe){=}NAr]_2$ (Ar = 4-tolyl) (X), which were obtained according to reaction 1, were used as ligands. In compound I the substituents around the CN double bonds may be in the cis or in the trans position; structures F–H are possible. NMR evidence excludes G, which requires two MeO signals, but does not allow a choice to be made between F and H, which both require only one MeO signal as observed. When the compound acts as a chelating ligand, structure F is the most likely.


F


G

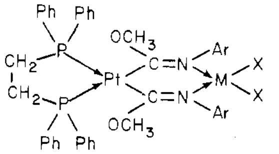

H

In compound X the arrangement of the four groups around the platinum atom cannot be established from the available data.[5] Both compounds I and X are potentially bidentate (chelating or bridging) ligands; furthermore compound X may yield additional information regarding the structure of the adducts with acceptor molecules due to the presence of the C≡N oscillator.

Both compounds are shown to be bifunctional bases since they could be diprotonated without cleavage of the metal–carbon bond[3] by acids whose conjugate bases are not good nucleophiles,[5] e.g., picric or fluoboric acids. In this way the stable, ionic bis(carbene) complexes II, III, and XI were obtained according to reaction 2b, while the carbene derivative IV, obtained through a different reaction, is discussed below. As required, new bands were found in the ir spectra above 3200 and around 1600 cm^{-1} and were assigned to the stretching and bending of the N—H bond. In addition, the C═N stretching vibration was lowered from the value observed in the ligand (ca. 1575 cm^{-1}) to ca. 1550 cm^{-1}. Correspondingly, additional signals, due to the NH$^+$ protons, could be found in the NMR spectra of all the compounds, including the picrate II for which N–H vibrations could not be detected in the infrared spectrum. Among the derivatives of the ligand X, protonation or complexation (see below) of the two nitrogen atoms brings about a shift to higher value (ca. 30 cm^{-1}) of the coordinated isocyanide stretching frequency. Analogous changes took place on protonation or on alkylation of other related molecules; e.g.,[14] starting from $[(Ph_3P)_2Pt(CNMe)\{C(OMe){=}NMe\}]^+$, where ν(C≡N) is at 2245 cm^{-1} and ν(C═N) is at 1626 cm^{-1}, protonation or alkylation gives ν(CN) at 2254 and 1592 cm^{-1} or 2260 and 1588 cm^{-1}, respectively.

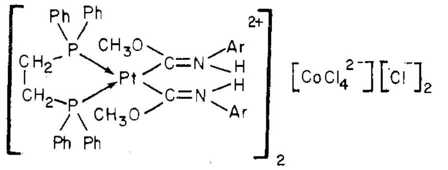
The donor properties of the ligands I and X were tested toward many acceptor centers, including those giving usually planar, linear, octahedral, or tetrahedral coordination (where bimetallocycles may be formed). While attempts are still being carried out, complete and positive results are reported for adducts with $CdBr_2$, CdI_2, $AgBF_4$, $CoCl_2$, $HgCl_2$, and $[Rh(CO)_2Cl]_2$.

By reaction of I with cobalt(II) chloride in anhydrous conditions, a blue, nonionic 1:1 adduct was obtained, VII, stable in dry solvents. In the paramagnetic, monomeric adduct, ν(C═N) was found at 1530 cm^{-1}, thus suggesting that both nitrogen atoms are engaged in complexation, while ν(Co—Cl) at 304 cm^{-1} and the visible spectrum gave evidence for tetrahedral coordination around the cobalt atom, as follows



V, M = Hg, X = Cl
VII, M = Co, X = Cl
VIII, M = Cd, X = Br
IX, Md = Cd, X = I

The 1:1 adduct obtained is stable only in anhydrous conditions. Indeed, if $CoCl_2{\cdot}6H_2O$ is employed, a blue carbene complex is obtained for which the formula is suggested from analytical and conductance data, magnetic moment ($4.4\ \mu_B$), and the electronic spectra (reflectance and $CHCl_3$ solution). No analytically pure compound has been obtained by reaction of X with anhydrous cobalt(II) chloride.



No carbene derivatives were obtained by the reaction of I with $CdBr_2{\cdot}4H_2O$ or with CdI_2. However, colorless 1:1 adducts were isolated, which on the basis of analytical data, molecular weight determinations, and low conductance values are formulated as VIII or IX. Correspondingly, these complexes show only one MeO and one *p*-Me signal in the NMR spectra and the ν(C=N) is displaced to ca. 1530 cm^{-1}.

Similarly, the same ligand I reacted with ethereal mercury(II) chloride, affording another 1:1 adduct, V, stable in the solid state but not in solution. The ir spectrum suggests that also in this case both nitrogen atoms are donors toward mercury, while a strong band at ca. 265 cm^{-1} may be assigned to terminal ν(Hg–Cl), a value to be compared with 273 cm^{-1} for (bpy)$HgCl_2$.[15] The compound is not stable in solution so that supporting evidence for the formula proposed was collected through the reaction

$$(Ph_2PCH_2)_2Pt[C(OMe){=}NAr]_2{\cdot}HgCl_2 + bpy \rightarrow (bpy)HgCl_2 + (Ph_2PCH_2)_2Pt[C(OMe){=}NAr]_2$$

The displacement and the recovery of the ligand I proves that neither mercuration of an aromatic ring nor oxidative addition of $HgCl_2$ on the square-planar species[16] took place.

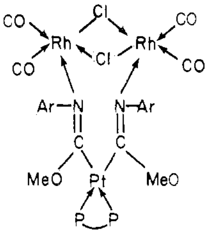
Under the same conditions the ligand X gives also a 1:1 adduct, XIIIa, which can be crystallized at room temperature from $CHCl_3/Et_2O$, yielding XIIIb, i.e. a species where 1 mol of $CHCl_3$ is clathrated, as evidenced by analytical and ir spectral data. The ir spectrum also shows that the ligand is probably monodentate, because two ν(C=N) stretching bands were observed, but only one of them was displaced from the value recorded in the free ligand, X. The NMR data ($CDCl_3$) indicate that the ligand molecule has not undergone any detectable change.

The ability of the potentially bidentate ligands, I and X, to bridge two other metal atoms was proved by treatment with $[Rh(CO)_2Cl]_2$, which is known to undergo bridge-splitting reactions with nitrogen ligands, affording four-coordinate derivatives, e.g.,[17] $[(CO)_2RhCl]_2 + 2Ar{-}CN = 2\textit{cis}{-}(CO)_2RhCl(NC{-}Ar)$. The reaction yielded the same type of adducts, according to the reaction

$$[(CO)_2RhCl]_2 + (\text{ligand})_2Pt[C(OMe){=}NAr]_2 = (\text{ligand})_2Pt\{C(OMe){=}NAr{\rightarrow}Rh(CO)_2Cl\}_2$$

VI or XIV

Such a structure in the solid state is supported by the infrared spectra: here ν(C=N) is shifted to lower wavelength, terminal Rh—Cl stretching bands are evident at 310 cm^{-1}, and two strong carbonyl vibrations are detected at about the same values as in *cis*-$(CO)_2RhCl(NCAr)$. Consequently, a structure such as K, which is analogous to that recently proposed[18] for an adduct between a porphyrin and $[(CO)_2RhCl]_2$, can be excluded even if both in the porphyrin adduct and in K the bite of the ligand would probably be roughly the same. In solution, compound VI is not stable, while compound XIV is only moderately stable. Ir spectra in $CHCl_3$ (Table I) show the same ν(C≡N) and ν(C=O) as the Nujol mull spectra, while in the NMR spectra (Table II) more resonances due to OCH_3 groups are observed than required by the presence of only one isomer. Further evidence for the formula proposed for compound VI can be obtained by the ligand displacement reaction

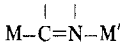


K

$$(Ph_2PCH_2)_2Pt[C(OMe){=}NAr{\rightarrow}Rh(CO)_2Cl]_2 + 4Ph_3P = 2CO + 2(Ph_3P)_2(CO)RhCl + (Ph_2PCH_2)_2Pt[C(OMe){=}NAr]_2$$

Last, a 1:1 adduct was obtained from VIII and $AgBF_4$; a polymeric structure involving the bridging ligand VIII is compatible with the presence of tetrahedral BF_4^- anion (ν(BF) at 1050 (vs, b) cm^{-1}).

In conclusion both ligands, I and X, are bifunctional bases and may act as bidentate ligands, although only I is shown to yield chelates. The complexes obtained from these organometallic ligands are more stable, at least toward storage, than the complexes obtained from the purely organic, homologous ligand ethyl *N*-*p*-tolylformimidate. The difference in gross stability, favoring the complex reported here, may be due to the chelate effect, when chelation takes place, or to electron delocalization on the system due to the presence of the double bond and to possible overlap of C=N π* orbitals with suitable orbitals of the metal atoms.[19]



$$M{-}\overset{|}{C}{=}\overset{|}{N}{-}M'$$

Additional evidence on the possibility of delocalization might come from x-ray evidence on the bond order between metal and carbon. Among metal–C(OR)=NR′ compounds no x-ray structure determination has been carried out, but on the related *trans*-PtI[C(Me)=N(*p*-ClC_6H_4)]$(PEt_3)_2$ complete data are available[20] and are discussed due to the lack of more direct evidence. In this compound the Pt–C distance is 2.027 (11) Å, to be compared with 1.98 (2) or 2.00 (3) Å in *cis*-$PtCl_2[C(OEt)NHPh]PEt_3$ or *trans*-$PtCl_2[C(NPhCH_2)_2]PEt_3$, respectively.[21] These values were taken as evidence for a certain amount of double bond between platinum and carbon.[21] Furthermore, direct evidence showing that two metal atoms can interact through an unsaturated CN bridging ligand is now available, e.g., in the ESR spectrum of the complex *trans*-$(Et_3P)_2HPtC{\equiv}N{\rightarrow}TiClCp_2$: here the magnitude of the hyperfine coupling to platinum suggests[22] that there is considerable electron delocalization from titanium to platinum through the unsaturated CN bond.

Registry No. I, 60209-63-4; II, 60195-65-5; III, 60195-66-6; IV, 60209-64-5; V, 60184-08-9; VI, 60183-98-4; VII, 60184-11-4; VIII, 60184-09-0; IX, 60184-10-3; X, 60251-48-1; XI, 60195-74-6; XIIIa, 60184-12-5; XIV, 60183-97-3; $[Rh(CO)_2Cl]_2$, 14523-22-9.

References and Notes

(1) (a) Financial support through Consiglio Nazionale delle Ricerche is acknowledged. (b) Milan University. (c) University of Camerino.
(2) G. Minghetti, F. Bonati, and M. Massobrio, *J. Chem. Soc., Chem. Commun.*, 260 (1973); *Inorg. Chem.*, **14**, 1974 (1975).
(3) G. Minghetti and F. Bonati, *Angew. Chem.*, **84**, 482 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 429 (1972); *Inorg. Chem.*, **13**, 1600 (1974).
(4) (a) G. Minghetti and F. Bonati, *Gazz. Chim. Ital.*, **102**, 205 (1972); (b) *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Natur., Rend.*, [8] **49**, 287 (1970).
(5) G. Minghetti, F. Bonati, and G. Banditelli, *Synth. Inorg. Met.-Org. Chem.*, **3**, 415 (1973).
(6) P. M. Treichel, *Adv. Organomet. Chem.*, **11**, 21 (1973).
(7) B. Crociani and T. Boschi, *J. Organomet. Chem.*, **24**, Cl (1970).
(8) F. Bonati and G. Minghetti, *J. Organomet. Chem.*, **60**, C43 (1973).
(9) M. J. Braithwaite and R. S. Nyholm, *J. Inorg. Nucl. Chem.*, **35**, 2237 (1973); R. W. Baker, M. J. Braithwaite, and R. S. Nyholm, *J. Chem. Soc., Dalton Trans.*, 1924 (1972).
(10) M. L. Brown, J. L. Cramer, J. A. Ferguson, T. J. Meyer, and N. Winterton, *J. Am. Chem. Soc.*, **94**, 8707 (1972).
(11) G. R. Newkome and G. L. McClure, *J. Am. Chem. Soc.*, **96**, 617 (1974).
(12) D. F. Evans, *J. Chem. Soc.*, 2002 (1959).
(13) G. Minghetti, G. Banditelli, and F. Bonati, *Inorg. Chim. Acta*, **12**, 85 (1975).
(14) P. M. Treichel, W. J. Knebel, and R. W. Hess, *J. Am. Chem. Soc.*, **93**, 5424 (1971).
(15) G. E. Coates and D. Ridley, *J. Chem. Soc.*, 166 (1964).
(16) E.g., R. S. Nyholm and K. Vrieze, *J. Chem. Soc.*, 5337 (1965).
(17) R. Ugo, F. Bonati, and M. Fiore, *Inorg. Chim. Acta*, **2**, 463 (1968); D. M. Lawson and G. Wilkinson, *J. Chem. Soc.*, 1900 (1965).
(18) H. Ogoshi, T. Omura, and Z. Yoshida, *J. Am. Chem. Soc.*, **95**, 1666 (1973).
(19) P. Jutzi, *Angew. Chem.*, **87**; 269 (1975); *Angew. Chem., Int. Ed. Engl.*, **14**, 232 (1975), and references therein.
(20) K. P. Wagner, P. M. Treichel, and J. C. Calabrese, *J. Organomet. Chem.*, **71**, 299 (1974), and references therein.
(21) F. A. Cotton and C. M. Lukehart, *Prog. Inorg. Chem.*, **16**, 487 (1972).
(22) L. Manzer and G. W. Parshall, *J. Chem. Soc., Chem. Commun.*, 227 (1975).

Contribution from the Department of Chemistry,
University of Nebraska, Lincoln, Nebraska 68588

Ligand-Exchange Reaction of Ethylenediaminetetraacetate and Ethylenediaminetetraacetatocuprate(II)[1]

R. KEN FORCÉ, ROBERT S. MARIANELLI, and JAMES D. CARR*

Received April 9, 1976 AIC60278+

The symmetric ligand exchange of EDTA with CuEDTA in deuterium oxide is measured by NMR line-broadening techniques from 7 to 94 °C. The ligand-exchange reaction is observed above ca. 56 °C; below this temperature, some other process causes the line width to increase. For the ligand-exchange reaction, $E_a = 10.8$ kcal/mol, $\log A = 9.6$, and the rate constant for unprotonated EDTA at 25 °C is 45 $M^{-1}\ s^{-1}$. In contrast to studies of other metal ions in analogous reactions, the rate constant of exchange of the monoprotonated EDTA is nearly equal to the value for the unprotonated ligand.

Introduction

Recently, several papers have appeared discussing the symmetric ligand-exchange reactions of EDTA (ethylenediaminetetraacetate ion or Y^{4-}) with a metal complex of EDTA (eq 1; the asterisk merely serves to distinguish the entering EDTA molecule from the leaving molecule), where M has been calcium,[2] cadmium,[3-5] lead,[6,7] strontium,[8] and nickel.[9] Nuclear magnetic resonance (NMR) line-broadening techniques were used to study the calcium, cadmium, lead, and strontium reactions. The nickel exchange reaction, a relatively slow reaction, was followed by NMR in which a deuterated ligand was exchanged with a nondeuterated complex.

$$\mathrm{EDTA}^{*4-} + \mathrm{M(EDTA)}^{2-} \rightleftarrows \mathrm{M(EDTA^*)}^{2-} + \mathrm{EDTA}^{4-} \qquad (1)$$

In this work, NMR line-broadening techniques were used to follow the ligand-exchange kinetics of EDTA with the copper complex of EDTA. More elaborate experimental procedures were required to study the kinetics of reaction 1 with the paramagnetic copper(II) ion than had been the case with previously studied diamagnetic metal ions. The pH dependency and activation parameters for the exchange reaction are measured and parallel pathways for both the tetraanion and the monoprotonated anion as the entering ligand are observed.

Experimental Section

All exchange reactions were carried out in deuterium oxide to prevent the H_2O signal from obscuring the much weaker signals of the EDTA solute. A stock solution of potassium deuterioxide was prepared by slowly adding small pieces of reagent grade potassium metal to deuterium oxide (99.77% D_2O, Columbia Organic Chemicals Co., Inc.) and standardized by titration with standard nitric acid.

Solid D_4EDTA (the ionizable hydrogens replaced by deuterium) was prepared by dissolving reagent grade disodium ethylenediaminetetraacetate dihydrate in deuterium oxide and then stripping off the solvent. Fresh deuterium oxide was added and the procedure was repeated three times. Anhydrous phosphorus pentoxide was then added to the solution of EDTA (to increase the acidity without adding hydrogen ion) until precipitation of the D_4EDTA was observed. The solid tetra acid was filtered, dried in an oven for 2 h at 110 °C, and stored in a desiccator over P_2O_5. Stock solutions of the tetradeuterio acid were prepared by dissolving the D_4EDTA in deuterium oxide, neutralizing with potassium deuterioxide and standardizing with standard copper solution using Snazox indicator.[10]

The rate of reaction 2 was measured by recording the NMR spectra of different solutions of CuEDTA in the presence of a measured excess of EDTA. Each solution contained approximately the same total, or analytical, concentration of EDTA and CuEDTA, but since the pD of each solution was different, different concentrations of the tetraanion of EDTA were present. Working solutions were prepared with the aid of a Gilmont microburet. All pD measurements were made at 25 °C with a Corning Model 12 pH meter equipped with a Corning semimicro combination electrode. The appropriate ΔpD correction, 0.46, as described previously,[11] was applied to the meter reading to obtain the correct pD values.

$$\mathrm{EDTA}^* + \mathrm{Cu(EDTA)}^{2-} \rightleftarrows \mathrm{EDTA} + \mathrm{Cu(EDTA^*)}^{2-} \qquad (2)$$

Relative concentrations of differently protonated species of EDTA were calculated from values of appropriate protonation constants. The pK_4 values used were measured in D_2O with the ionic strength controlled at 2.0 (KCl). The values at 25 and 35 °C were found to be 10.36 and 10.18, respectively. Values at higher temperatures were calculated using the reported ΔH of ionization of EDTA[12] and the measured pK_4. It was assumed that the ΔH of ionization of EDTA was the same in protium oxide and deuterium oxide. (The following pK_4 values were obtained: 9.36 (94 °C), 9.45 (85 °C), 9.72 (65 °C), 9.86 (56 °C), 10.25 (31 °C), 10.36 (25 °C), 10.70 (7 °C)).