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ORGANOMETALLIC COMPLEXES WITH METAL—METAL BONDS

XII *. A TRIMETALLIC CARBENE COMPLEX WITH Mo—Pt—Mo BONDS. PREPARATION AND STRUCTURE OF *trans*-$Pt(C_6H_{11}NC)(C_6H_{11}NHCOC_2H_5)[Mo(CO)_3\text{-}\eta^5\text{-}C_5H_5]_2$

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Summary

The linear trimetallic title complex is formed from *cis*-$Cl_2Pt(CNC_6H_{11})[C(OC_2H_5)(NHC_6H_{11})]$ and $NaMoCp(CO)_3$. It has been characterized by IR-spectral data and by a crystal structure determination. The metal—metal stretching frequency of 156 cm^{-1} and the Pt—Mo distances of 288.9 pm indicate relatively strong Pt—Mo bonding.

The electronic and stereochemical factors influencing the reactions which lead to metal—metal bonds are far from being well understood [1]. We have therefore initiated a systematic and cooperative study with the aim of gaining more insight into control over such reactions for preparative purposes. As part of this study we have investigated the nucleophilic substitution of halide ligands by carbonyl metalate anions M^- ($M = Co(CO)_4$, $Mn(CO)_5$, $CpMo(CO)_3$) in PtL_2Cl_2 complexes.

The nature of the ligand L plays a major role in determining the structure of the reaction products. Where L is a pyridine type of ligand, linear trimetallic complexes M—PtL_2—M are obtained [2,3]. Where L is a tertiary phosphine, ligand exchange occurs between the metals Pt and M and new tetra- or pentametallic clusters are formed [4,5]. Isonitrile ligands L can serve as spectroscopic probes for electronic effects across the Pt—M bonds, as was shown for the linear trimetallic M—$Pt(CNR)_2$-M complexes [6].

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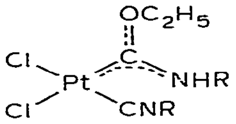
* Part XI: see ref. 6.

As an extension of this work we have carried out reactions between the carbene(isonitrile)platinum complex (I) and carbonyl metalates. Only few bimetallic transition metal complexes bearing a terminal carbene ligand are known (with Mn—Mn [7,8] or Tc—Tc, Re—Re, Mn—Re [9] metal—metal bonds), together with some carbene complexes involving a bond between a transition metal and a post-transition metal (with Sn—Co, Pb—Co [10] or Ge—Mn [11] Ge—Mo, Ge—W, Sn—Mo, Sn—W [12] or Sn—Pd—Sn, Sn—Pt—Sn [13] bonds). So far, no carbene complex with metal—metal bond(s) between platinum and a transition metal has been reported. It was therefore open to speculation whether trimetallic chains or more complicated clusters would result from these reactions. This paper describes the results of the reaction of I with CpMo(CO)$_3^-$.



(I) R = C$_6$H$_{11}$

Experimental

All manipulations were carried out under nitrogen in freshly distilled and deoxygenated solvents. The starting complex I was prepared according to the published method [13].

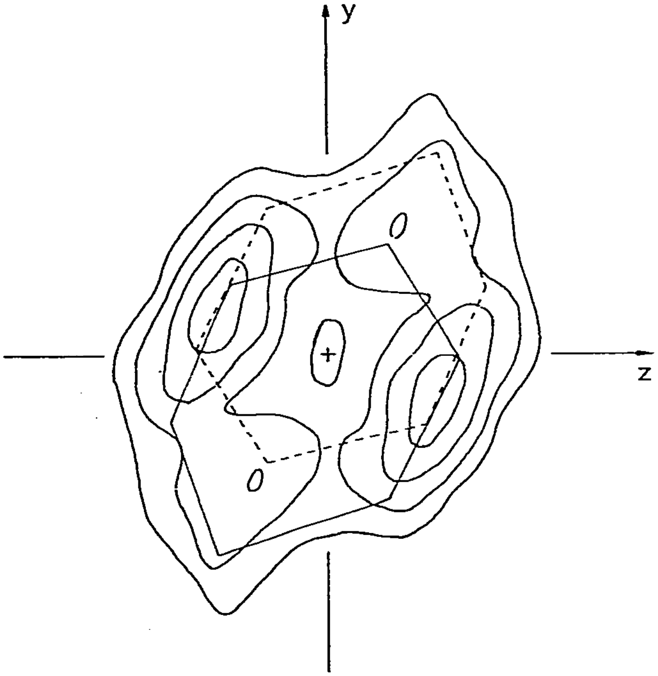


Fig. 1. Electron density and location of C$_6$H$_{12}$ molecules in the yz plane around the center of symmetry at (0, 1/2, 0).

cis-(Cyclohexylisocyanido)[ethoxy(cyclohexylamino)carbene] bis(η^5-cyclopentadienyltricarbonylmolybdato)platinum(II) (II)

To a suspension of I (0.48 g, 0.9 mmol) in 15 ml THF at —70°C is added a

TABLE 1

ATOMIC COORDINATES OF II

Atom	*X*	*Y*	*Z*
Pt	0.2871(1)	0.4818(1)	0.3602(1)
Mo(1)	0.2354(1)	0.7039(1)	0.3574(1)
Mo(2)	0.3267(1)	0.2573(1)	0.3598(1)
C(1a)	0.2304(8)	0.4537(8)	0.4215(4)
O(1)	0.1303(6)	0.4286(7)	0.4047(3)
C(8)	0.0527(11)	0.4184(15)	0.3362(6)
C(9)	—0.0489(16)	0.4394(31)	0.3271(10)
N(1a)	0.2928(7)	0.4626(8)	0.4852(4)
C(2a)	0.2517(10)	0.4553(11)	0.5326(5)
C(3a)	0.2523(13)	0.3408(12)	0.5532(7)
C(4a)	0.2103(16)	0.3403(15)	0.6038(8)
C(5a)	0.2835(15)	0.4091(18)	0.6609(7)
C(6a)	0.2828(16)	0.5242(18)	0.6387(8)
C(7a)	0.3264(12)	0.5274(14)	0.5901(5)
C(1b)	0.3402(9)	0.5079(10)	0.2985(5)
N(1b)	0.3670(8)	0.5213(8)	0.2608(4)
C(2b)	0.3879(10)	0.5361(12)	0.2070(5)
C(3b)	0.4078(14)	0.4250(13)	0.1873(6)
C(4b)	0.4216(15)	0.4400(14)	0.1271(7)
C(5b)	0.3208(15)	0.4888(16)	0.0730(6)
C(6b)	0.3026(15)	0.5989(16)	0.0937(7)
C(7b)	0.2873(13)	0.5880(14)	0.1540(6)
C(11)	0.3894(12)	0.6659(11)	0.3944(5)
O(11)	0.4798(8)	0.6582(8)	0.4174(4)
C(12)	0.2759(13)	0.7841(11)	0.3042(6)
O(12)	0.3005(11)	0.8311(10)	0.2708(6)
C(13)	0.1475(12)	0.6274(14)	0.2772(7)
O(13)	0.0876(9)	0.5899(11)	0.2274(5)
C(14)	0.1548(17)	0.6944(14)	0.4249(9)
C(15)	0.2535(17)	0.7497(14)	0.4580(8)
C(16)	0.2426(17)	0.8457(13)	0.4220(9)
C(17)	0.1349(17)	0.8426(16)	0.3661(8)
C(18)	0.0810(15)	0.7503(15)	0.3673(8)
C(21)	0.2245(13)	0.3111(13)	0.2753(7)
O(21)	0.1599(9)	0.3337(9)	0.2222(5)
C(22)	0.4206(12)	0.2506(11)	0.3229(6)
O(22)	0.4760(10)	0.2447(9)	0.3003(5)
C(23)	0.4292(9)	0.3646(10)	0.4148(5)
O(23)	0.5048(7)	0.4075(8)	0.4553(4)
C(24)	0.2382(19)	0.1817(12)	0.4130(10)
C(25)	0.2063(15)	0.1245(15)	0.3542(9)
C(26)	0.3017(18)	0.0754(12)	0.3598(10)
C(27)	0.3895(15)	0.1034(13)	0.4217(9)
C(28)	0.3508(17)	0.1700(14)	0.4539(8)
C(31)	—0.0054(41)	0.5569(54)	0.0631(25)
C(32)	0.0014(34)	0.6654(39)	0.0450(21)
C(3)	—0.0047(39)	0.6208(47)	—0.0241(30)
C(34)	—0.0062(30)	0.5061(53)	—0.0526(20)
C(35)	—0.0047(32)	0.4099(40)	—0.0234(25)
C(36)	—0.0008(29)	0.4391(50)	0.0387(18)

solution of $NaMo(CO)_3$-η^5-Cp (1.8 mmol) in 30 ml THF. The solution immediately turns orange and is left under agitation at −20°C for 1 h. The solvent is removed under reduced pressure and the residue is extracted with toluene. The toluene

TABLE 2

TEMPERATURE FACTORS OF II

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pt	3.61(2)	3.76(3)	2.57(1)	0.20(2)	1.78(1)	0.00(2)
Mo(1)	5.30(6)	4.14(6)	3.54(5)	1.23(5)	2.48(4)	0.57(4)
Mo(2)	5.22(6)	3.67(6)	4.31(5)	−0.41(5)	2.90(5)	−0.58(4)
C(1a)	3.6(5)	3.4(6)	3.0(4)	0.7(4)	1.9(4)	0.0(4)
O(1)	3.7(4)	7.8(6)	4.0(4)	−0.6(4)	2.3(3)	−0.6(4)
C(8)	4.0(7)	11.3(13)	3.7(6)	−0.5(7)	0.8(5)	−1.5(7)
C(9)	5.3(11)	33.5(40)	7.4(12)	−0.3(17)	0.8(10)	−4.2(18)
N(1a)	4.6(5)	5.1(7)	3.2(4)	−0.2(4)	2.4(4)	−0.2(4)
C(2a)	5.0(6)	6.7(9)	3.4(5)	0.1(6)	2.9(5)	0.3(5)
C(3a)	8.9(10)	6.4(10)	6.2(8)	0.6(8)	5.6(8)	1.3(7)
C(4a)	11.7(13)	9.2(12)	7.2(10)	−0.2(10)	7.1(10)	0.2(9)
C(5a)	9.6(19)	12.6(15)	5.4(8)	0.9(11)	5.3(9)	1.6(9)
C(6a)	12.7(14)	12.9(16)	6.6(9)	−1.2(13)	7.6(10)	−2.1(10)
C(7a)	8.5(9)	9.5(11)	3.2(5)	−1.7(8)	3.6(6)	−1.4(6)
C(1b)	4.4(5)	4.9(7)	3.3(5)	0.0(8)	2.2(4)	0.2(5)
N(1b)	5.8(5)	5.2(6)	3.7(4)	−0.9(5)	3.2(4)	−0.4(4)
C(2b)	5.9(7)	7.6(9)	2.9(5)	0.5(6)	3.0(5)	0.6(5)
C(3b)	11.6(12)	7.2(10)	5.5(8)	2.5(9)	6.7(9)	1.1(7)
C(4b)	11.6(13)	9.2(12)	6.2(9)	2.5(10)	6.8(10)	0.9(8)
C(5b)	10.7(12)	10.8(14)	3.8(6)	0.7(11)	3.9(8)	−0.6(8)
C(6b)	10.3(12)	10.3(14)	5.0(8)	1.8(10)	5.0(8)	2.4(8)
C(7b)	7.7(9)	10.0(12)	4.6(7)	1.6(8)	3.8(7)	2.3(7)
C(11)	5.9(8)	5.3(8)	2.9(5)	0.4(6)	1.6(5)	−0.2(5)
O(11)	4.6(5)	7.4(7)	5.6(5)	−0.4(5)	1.2(4)	−0.6(5)
C(12)	8.2(10)	3.9(8)	4.6(7)	2.2(7)	2.6(7)	1.0(6)
O(12)	12.1(9)	9.1(9)	9.1(8)	2.6(7)	7.2(7)	4.4(7)
C(13)	5.1(8)	9.1(12)	4.8(7)	0.8(7)	2.5(6)	0.1(7)
O(13)	7.1(7)	12.5(10)	4.6(5)	1.7(6)	0.9(5)	−1.3(6)
C(14)	11.0(13)	7.3(11)	8.5(11)	4.0(10)	8.0(11)	1.3(9)
C(15)	11.3(14)	6.2(11)	6.2(9)	2.1(10)	5.9(10)	0.3(8)
C(16)	13.1(15)	4.8(10)	8.4(11)	−1.3(9)	8.4(12)	−2.4(8)
C(17)	10.2(13)	7.5(12)	7.0(10)	4.2(10)	5.8(10)	0.9(9)
C(18)	10.3(13)	6.5(11)	8.1(11)	4.1(10)	6.3(10)	2.0(9)
C(21)	6.9(9)	7.6(10)	4.8(7)	−3.2(8)	2.6(7)	−2.7(7)
O(21)	8.1(7)	8.8(8)	4.9(5)	−2.3(6)	0.3(5)	−0.8(5)
C(22)	7.1(9)	5.6(8)	5.3(5)	1.3(6)	3.7(5)	0.1(5)
O(22)	10.2(8)	8.7(8)	9.4(7)	3.3(6)	7.7(7)	2.0(6)
C(23)	3.4(6)	5.3(7)	3.4(5)	−0.1(5)	1.6(4)	0.1(5)
O(23)	4.2(5)	6.4(6)	5.0(5)	−0.1(4)	1.0(4)	0.5(4)
C(24)	13.4(16)	3.6(9)	10.0(12)	−2.8(9)	9.1(12)	−1.0(8)
C(25)	8.3(11)	5.8(11)	9.7(12)	−2.9(9)	4.7(10)	0.7(9)
C(26)	11.1(14)	3.4(8)	10.0(12)	−1.0(9)	7.0(12)	−0.5(8)
C(27)	9.5(12)	4.9(10)	8.9(11)	0.7(8)	6.0(11)	2.7(8)
C(28)	9.4(12)	6.6(11)	8.1(11)	−0.5(9)	5.9(10)	2.1(8)
C(31)	11(2)					
C(32)	10(1)					
C(33)	11(2)					
C(34)	7(1)					
C(35)	8(1)					
C(36)	6(1)					

solution is filtered, and addition of pentane causes the orange product II (0.52 g, yield 61%, m.p. 161°C, dec.) to precipitate. (Found.: C, 40.7; H, 4.2; N, 2.9; $C_{32}H_{38}N_2O_7Mo_2Pt$ calcd.: C, 40.47; H, 4.03; N, 2.95%.)

A crystalline material containing cyclohexane was obtained by recrystallization from toluene/cyclohexane. Crystal data: $C_{32}H_{38}N_2O_7Mo_2Pt \cdot 0.5\ C_6H_{12}$, M 949.6 + 42, monoclinic, a 1430.6(3), b 1260.9(5), c 2381.9(3) pm, β 119.11(2)°, V 3.754 nm^3, $d_{calc.}$ 1.76 for $Z = 4$, $d_{obs.}$ 1.76 g/cm^3, space group $P2_1/c$, Mo-K_α radiation, μ 48.8 cm^{-1}, 4113 absorption-corrected independent reflexions with $I > 2\sigma(I)$.

The molecule of II was located and refined by Patterson, Fourier, and least squares methods. Anisotropic refinement without inclusion of the cyclohexane C atoms converged at an R value (unit weights) of 0.051. The disordered cyclo-

TABLE 3

ATOMIC DISTANCES IN II

Bond	Length (pm)	Bond	Length (pm)
Pt—Mo(1)	288.9(2)	C(1b)—N(1b)	115(2)
Pt—Mo(2)	288.9(2)	N(1b)—C(2b)	146(2)
Pt—C(1a)	202(1)	C(2b)—C(3b)	155(2)
Pt—C(1b)	198(2)	C(3b)—C(4b)	155(3)
Pt—C(23)	233(1)	C(4b)—C(5b)	152(2)
		C(5b)—C(6b)	154(3)
Mo(1)—C(11)	199(2)	C(6b)—C(7b)	156(3)
Mo(1)—C(12)	192(2)	C(7b)—C(2b)	153(2)
Mo(1)—C(13)	196(2)		
Mo(1)—C(14)	240(3)	C(14)—C(15)	142(3)
Mo(1)—C(15)	236(2)	C(15)—C(16)	145(3)
Mo(1)—C(16)	233(2)	C(16)—C(17)	147(3)
Mo(1)—C(17)	234(2)	C(17)—C(18)	140(3)
Mo(1)—C(18)	241(3)	C(18)—C(14)	144(2)
Mo(2)—C(21)	195(1)	C(24)—C(25)	144(3)
Mo(2)—C(22)	193(2)	C(25)—C(26)	144(4)
Mo(2)—C(23)	196(1)	C(26)—C(27)	144(3)
Mo(2)—C(24)	238(3)	C(27)—C(28)	142(4)
Mo(2)—C(25)	236(2)	C(28)—C(24)	143(3)
Mo(2)—C(26)	232(2)		
Mo(2)—C(27)	234(2)	C(11)—O(11)	114(2)
Mo(2)—C(28)	237(2)	C(12)—O(12)	117(3)
		C(13)—O(13)	117(2)
C(1a)—O(1)	132(2)		
O(1)—C(8)	147(1)	C(21)—O(21)	118(2)
C(8)—C(9)	137(3)	C(22)—O(22)	116(3)
		C(23)—O(23)	117(1)
C(1a)—N(1a)	134(1)		
N(1a)—C(2a)	151(2)		
C(2a)—C(3a)	153(2)	C(31)—C(32)	145(9)
C(3a)—C(4a)	159(3)	C(32)—C(33)	170(9)
C(4a)—C(5a)	152(2)	C(33)—C(34)	159(9)
C(5a)—C(6a)	154(3)	C(34)—C(35)	139(8)
C(6a)—C(7a)	156(3)	C(35)—C(36)	150(8)
C(7a)—C(2a)	156(2)	C(36)—C(31)	161(9)

TABLE 4

BOND ANGLES IN II

Angle	Degrees	Angle	Degrees	Angle	Degrees	Angle	Degrees
1. At Pt		C(14)—Mo(1)—C(18)	35.0(6)	C(24)—Mo(2)—C(27)	58.2(8)	*6. At the C(CO) atoms*	
Mo(1)—Pt—Mo(2)	176.93(4)	C(15)—Mo(1)—C(16)	36.0(7)	C(24)—Mo(2)—C(28)	35.0(7)	Mo(1)—C(11)—O(11)	171(1)
Mo(1)—Pt—C(1a)	90.0(3)	C(15)—Mo(1)—C(17)	59.6(7)	C(25)—Mo(2)—C(26)	35.9(9)	Mo(1)—C(12)—O(12)	178(1)
Mo(1)—Pt—C(1b)	90.5(4)	C(15)—Mo(1)—C(18)	59.5(6)	C(25)—Mo(2)—C(27)	59.5(7)	Mo(1)—C(13)—O(13)	173(2)
Mo(2)—Pt—C(1a)	88.8(3)	C(16)—Mo(1)—C(17)	36.7(6)	C(25)—Mo(2)—C(28)	59.3(7)	Mo(2)—C(21)—O(21)	173(1)
Mo(2)—Pt—C(1b)	90.8(4)	C(16)—Mo(1)—C(18)	59.7(8)	C(26)—Mo(2)—C(27)	36.1(6)	Mo(2)—C(22)—O(22)	179(1)
C(1a)—Pt—C(1b)	178.8(4)	C(17)—Mo(1)—C(18)	34.4(8)	C(26)—Mo(2)—C(28)	59.5(8)	Mo(2)—O(23)—O(23)	164(1)
				C(27)—Mo(2)—C(28)	35.1(9)		
2. At Mo(1)							
Pt—Mo(1)—C(11)	62.7(4)	*3. At Mo(2)*				*7. At the C(Cp) atoms*	
Pt—Mo(1)—C(12)	111.8(5)	Pt—Mo(2)—C(21)	67.1(5)	*4. Within the carbene ligand*		Mo(1)—C(14)—C(18)	71(2)
Pt—Mo(1)—C(13)	65.2(5)	Pt—Mo(2)—C(22)	103.0(5)	Pt—C(1a)—N(1a)	121.6(9)	Mo(1)—C(14)—C(15)	73(2)
Pt—Mo(1)—C(14)	97.9(5)	Pt—Mo(2)—C(23)	53.4(4)	Pt—C(1a)—O(1)	125.5(7)	Mo(1)—C(15)—C(14)	74(1)
Pt—Mo(1)—C(15)	108.3(5)	Pt—Mo(2)—C(24)	103.6(5)	N(1a)—C(1a)—O(1)	113(1)	Mo(1)—C(15)—C(16)	71(1)
Pt—Mo(1)—C(16)	143.1(5)	Pt—Mo(2)—C(25)	123.9(5)	C(1a)—O(1)—C(8)	119(1)	Mo(1)—C(16)—C(15)	73(1)
Pt—Mo(1)—C(17)	152.2(6)	Pt—Mo(2)—C(26)	159.7(7)	O(1)—C(8)—C(9)	110(2)	Mo(1)—C(16)—C(17)	72(1)
Pt—Mo(1)—C(18)	118.0(5)	Pt—Mo(2)—C(27)	145.9(5)	C(1a)—N(1a)—C(2a)	124(1)	Mo(1)—C(17)—C(16)	71(1)
C(11)—Mo(1)—C(12)	78.2(7)	Pt—Mo(2)—C(28)	113.0(5)	N(1a)—C(2a)—C(3a)	111(1)	Mo(1)—C(17)—C(18)	75(1)
C(11)—Mo(1)—C(13)	111.2(7)	C(21)—Mo(2)—C(22)	83.3(7)	N(1a)—C(2a)—C(7a)	106(1)	Mo(1)—C(18)—C(17)	70(1)
C(11)—Mo(1)—C(14)	118.7(6)	C(21)—Mo(2)—C(23)	113.1(6)	C(2a)—C(3a)—C(4a)	108(1)	Mo(1)—C(18)—C(14)	72(1)
C(11)—Mo(1)—C(15)	93.3(7)	C(21)—Mo(2)—C(24)	111.3(8)	C(3a)—C(4a)—C(5a)	109(2)	Mo(2)—C(24)—C(28)	72(2)
C(11)—Mo(1)—C(16)	102.0(7)	C(21)—Mo(2)—C(25)	91.7(7)	C(3a)—C(4a)—C(5a)	110(1)	Mo(2)—C(24)—C(25)	71(2)
C(11)—Mo(1)—C(17)	137.4(6)	C(21)—Mo(2)—C(26)	107.9(7)	C(4a)—C(5a)—C(6a)	110(2)	Mo(2)—C(25)—C(24)	73(1)
C(11)—Mo(1)—C(18)	152.3(6)	C(21)—Mo(2)—C(27)	143.9(6)	C(5a)—C(6a)—C(7a)	107(1)	Mo(2)—C(25)—C(26)	71(1)
C(12)—Mo(1)—C(13)	82.7(7)	C(21)—Mo(2)—C(28)	146.3(8)	C(6a)—C(7a)—C(2a)	107(1)	Mo(2)—C(26)—C(25)	73(1)
C(12)—Mo(1)—C(14)	150.3(7)	C(22)—Mo(2)—C(23)	82.8(6)	C(7a)—C(2a)—C(3a)	112(1)	Mo(2)—C(26)—C(27)	73(1)
C(12)—Mo(1)—C(15)	128.7(7)	C(22)—Mo(2)—C(24)	153.1(7)			Mo(2)—C(27)—C(26)	71(1)
C(12)—Mo(1)—C(16)	95.8(8)	C(22)—Mo(2)—C(25)	126.4(7)	*5. Within the isonitrile ligand*		Mo(2)—C(27)—C(28)	74(1)
C(12)—Mo(1)—C(17)	93.5(8)	C(22)—Mo(2)—C(26)	95.6(9)	Pt—C(1b)—N(1b)	177.1(9)	Mo(2)—C(28)—C(27)	71(1)
C(12)—Mo(1)—C(18)	121.6(7)	C(22)—Mo(2)—C(27)	96.4(8)	C(1b)—N(1b)—C(2b)	173(1)	Mo(2)—C(28)—C(24)	73(1)
C(13)—Mo(1)—C(14)	109.8(7)	C(22)—Mo(2)—C(28)	126.7(7)	N(1b)—C(2b)—C(3b)	107(1)	C(14)—C(15)—C(16)	107(1)
C(13)—Mo(1)—C(15)	144.6(8)	C(23)—Mo(2)—C(24)	109.9(6)	N(1b)—C(2b)—C(7b)	106(1)	C(15)—C(16)—C(17)	106(2)
C(13)—Mo(1)—C(16)	145.6(7)	C(23)—Mo(2)—C(25)	144.9(7)	C(2b)—C(3b)—C(4b)	107(1)	C(16)—C(17)—C(18)	110(2)
C(13)—Mo(1)—C(17)	108.9(7)	C(23)—Mo(2)—C(26)	138.5(6)	C(3b)—C(4b)—C(5b)	110(2)	C(17)—C(18)—C(14)	106(2)
C(13)—Mo(1)—C(18)	91.7(7)	C(23)—Mo(2)—C(27)	102.7(5)	C(4b)—C(5b)—C(6b)	109(1)	C(18)—C(14)—C(15)	111(2)
C(14)—Mo(1)—C(15)	34.8(7)	C(23)—Mo(2)—C(28)	88.4(6)	C(5b)—C(6b)—C(7b)	110(2)	C(24)—C(25)—C(26)	107(2)
C(14)—Mo(1)—C(16)	58.4(8)	C(24)—Mo(2)—C(25)	35.3(7)	C(6b)—C(7b)—C(2b)	108(2)	C(25)—C(26)—C(27)	108(2)
C(14)—Mo(1)—C(17)	57.3(8)	C(24)—Mo(2)—C(26)	58.9(9)	C(7b)—C(2b)—C(3b)	112(1)	C(26)—C(27)—C(28)	109(2)
						C(27)—C(28)—C(24)	107(2)
						C(28)—C(24)—C(25)	109(2)

hexane molecules placed around centers of symmetry could only partially be located. They were found and refined as planar (due to the center of symmetry) distorted six-membered rings according to Fig. 1. The final *R* value was 0.042. The final difference Fourier map showed residual peaks smaller than ± 0.9×10^{-6} e/pm^3. Tables 1—4 give a listing of the structural data.

Description of the structure

Figure 2 shows the shape of the molecules of II. The almost ideal square planar environment about the platinum atom is provided by the two Mo atoms at 288.9 pm each, the isonitrile C atom at 198 pm and the carbene C atom at 202 pm. The isonitrile ligand is almost linearly coordinated (angles 177° at C(1b) and 174° at N(1b)) and has normal bond lengths. The carbene ligand *trans* to the isonitrile ligand has the expected planar geometry about the sp^2 *C*(1a) [14] and lies approximately at right angles (87°) to the PtL$_2$Mo$_2$ plane. The C(8)—C(9) bond seems to be deceptively short due to the high thermal motion of C(9). The CpMo(CO)$_3$ units may be called normal with terminal CO groups [15]. However, the CO group C(23)—O(23) (Mo—C 196 ppm, Pt—C 233 pm, Mo—C—O 164°) is approaching the semibridging state [16]. The other Pt—C(CO) distances (Pt—C(21) 265 pm, Pt—C(11) 273 pm, Pt—C(13) 279 pm) are in the expected range.

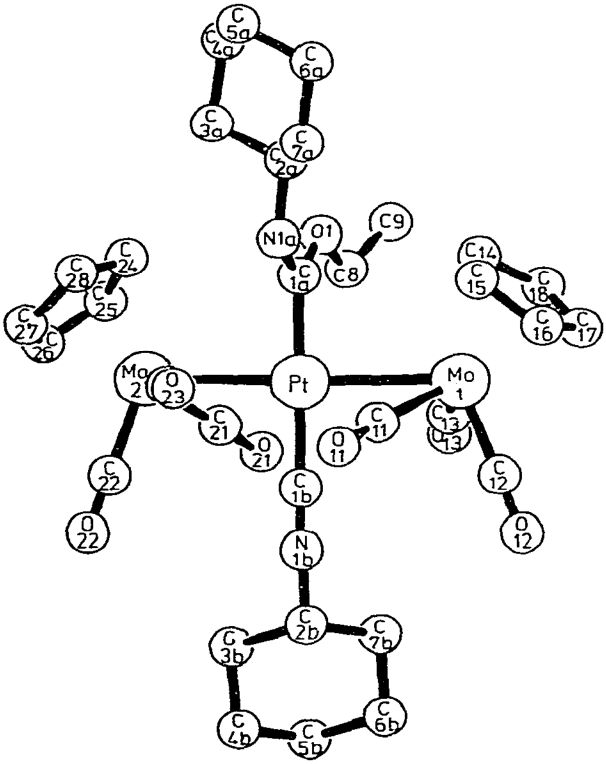
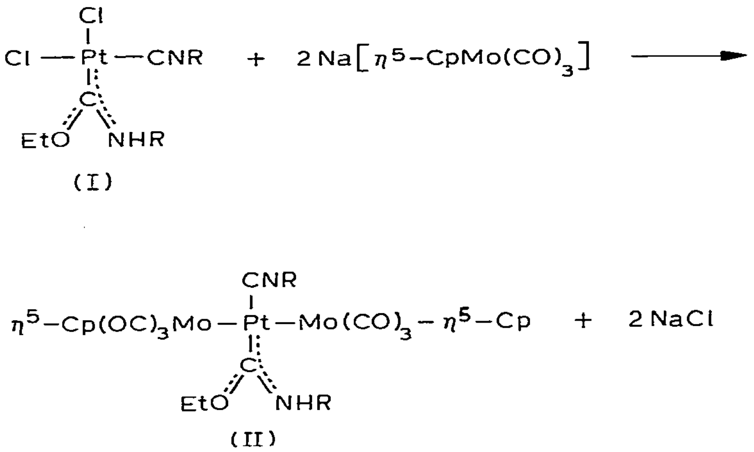


Fig. 2. Molecular structure of II. In order to improve the visibility of the carbene ligand, the projection is such that Mo(1) is above and Mo(2) below the plane.

Discussion

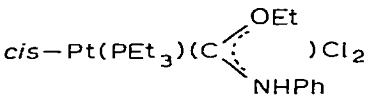
We find that the nucleophilic substitution reaction 1 occurs with *cis→trans* isomerization at the platinum atom.



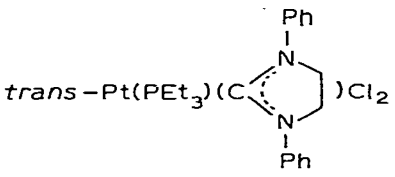
(I) (II) (1)

A similar result has already been found with the bis-pyridine- and bis-isonitrile-platinum complexes [6]. This isomerization is here particularly striking since the carbene complex I is known only in the *cis* form and has no tendency to isomerize to the *trans*-isomer. The *trans* arrangement in II is confirmed by a strong IR absorption at 156 cm^{-1} which can be unambigously assigned to the typical ν_{as}(Pt—Mo) stretching vibration of a linear trimetallic system [17]. The structure of II is significant since it is the first example of a carbene complex containing metal—metal bonds between platinum and a transition metal. Furthermore, this structure provides the first determination of a Pt—Mo bond length.

The Pt—C carbene bond length of 202 pm is close to the values for III (196 pm) [14] and IV (200 pm) [18]. The slight lengthening observed in our case is probably related to the *trans* influence of the isonitrile ligand. Nevertheless, the distance remains shorter than the expected Pt—C(sp^2) bond length of 204 pm [19], indicating in our case some degree of π-bonding. Similarly, the Pt—C (1b) distance (198 pm) is shorter than the expected Pt—C(sp) bond length (202 pm) [19]. The carbon—oxygen and carbon—nitrogen distances (132 and 134 pm) within the carbene ligand are very close to the values found in complex III (133 pm) [14].



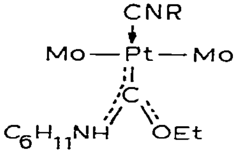
(III)



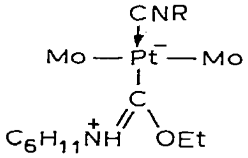
(IV)

We found recently that the ν(C≡N) frequency decreases markedly on going from *trans*-$Pt(C_6H_{11}NC)_2I_2$ (2230 cm^{-1}) to *trans*-$Pt(C_6H_{11}NC)_2$ $[Mo(CO)_3\text{-}\eta^5\text{-}Cp]_2$

(V) (2188 cm^{-1}) [6]. This is attributable to the donor properties of the metal carbonyl group, although σ- and π-contributions cannot be easily distinguished. Such an interpretation certainly applies to the lowering of the ν(C=N) frequency on passing from I (2230 cm^{-1}) to II (2208 cm^{-1}) whereas the σ-donor properties [20] and the higher *trans*-influence of the carbene ligand compared to the isonitrile ligand [21] accounts well for a higher ν(C≡N) frequency in II compared to V. The overall effect of replacing Cl in I by the better donor group $Mo(CO)_3$-η^5-Cp in II and of having Cl or RNC in *trans* position with respect to the carbene ligand in I and respectively II, is a lowering of the $\nu(C_{carbene}—N)$ frequency from 1572 cm^{-1} in I to 1534 cm^{-1} in II. The ν(NH) frequency in II at 3370 cm^{-1} is much higher than in I (3240 cm^{-1}) or in III (3130 cm^{-1}) [14] but very close to the value found in $(OC)_5CrC(CH_3)NH(CH_2Ph)$ (3378 cm^{-1}) [22]. These observations are indicative of a typical carbene ligand in II (form A), rather than of a contribution of the ylide form B.



(A)



(B)

The IR spectrum of II in the ν(CO) region, cf. Table 5, shows great similarity to that of *trans*-$Pt(3\text{-}MePy)_2[Mo(CO)_3\text{-}\eta^5\text{-}Cp]_2$ previously reported [3] (see Table 5). The number of ν(CO) bands, resp. 5 and 4, precludes an IR analysis based on local C_s symmetry about the Mo atom (expected IR active modes: $2A' + A''$). The indicated lowering of the local symmetry is confirmed especially at Mo(2)—C(23)—O(23), by the crystal structure analysis. Furthermore the possibility of rotamers [23] exists.

The metal—metal stretching frequency at 156 cm^{-1} in II is higher than that found at 140 cm^{-1} for the $Pt(3\text{-}MePy)_2[Mo(CO)_3Cp]_2$ complex [24]. The strengthening of the Pt—Mo bond may be related to the presence of electron π-accepting ligands on the platinum atom [6].

The Pt—Mo bond length of 288.9 pm in II is the first value observed for such a bond. It is shorter than the sum of the atomic radius of Pt (129.5 pm) [25] and the covalent radius of Mo (162 pm) taken as half the Mo—Mo distance in $[CpMo(CO)_3]_2$ [26]. The Pt—Mo distance can be compared to the Pt—Co and Pt—Mn bond lengths of respectively 261.3 and 274.3 pm in the $Pt(C_5H_5N)_2[Co(CO)_4]_2$ and $Pt(C_5H_5N)_2[Mn(CO)_5]_2$ complexes [27].

In comparing the formation of II with that of the other polymetallic Pt—M

TABLE 5

IR SPECTRA IN THE ν(CO) REGION (cm^{-1}) [a]

trans-$Pt(3\text{-}MePy)_2[Mo(CO)_3\text{-}\eta^5\text{-}Cp]_2$	(*a*) 1958m	1900vs		1835vs	1775vs
	(*b*) 1954f	1924m	1890s	1831s	
II	(*a*) 1945s	1904m	1849vs	1832(sh)	1781m

[a] (*a*) KBr pellet; (*b*) $CHCl_3$ solution.

complexes it must be noted that although the *cis*→*trans* rearrangement from 1 to II indicates mobility of the carbene or isonitrile ligands, no complete ligand dissociation and formation of clusters like with PR_3 ligand occurs.

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