Journal of Organometallic Chemistry, 205 (1981) 273—279
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

CATIONIC η^3-TRIPHENYLCYCLOPROPENYLNICKEL COMPLEXES WITH TRIDENTATE LIGANDS CONTAINING N, P, As AS THE DONOR ATOMS. MOLECULAR STRUCTURE OF η^3-TRIPHENYLCYCLOPROPENYL-1,1,1-TRIS(DIPHENYLPHOSPHINOMETHYL)ETHANENICKEL PERCHLORATE

C. MEALLI, S. MIDOLLINI, S. MONETI and L. SACCONI*

Istituto di Chimica Generale ed Inorganica, Università, Istituto Composti di Coordinazione del CNR, 39 via J. Nardi, 50132 Firenze (Italy)

(Received July 29th, 1980)

Summary

The $[(C_3Ph_3)Ni(PPh_3)_2]ClO_4$ complex reacts with the tridentate ligands, 1,1,1-tris(dimethylphosphinomethyl)ethane, 1,1,1-tris(diphenylphosphinomethyl)-ethane, (bis(2-diphenylphosphino)ethyl)phenylphosphine, (bis(2-diphenylphosphino)ethyl)-n-propylamine, and 1,1,1-tris(diphenylarsinomethyl)ethane to give cationic η^3-triphenylcyclopropenyl complexes of formula $[(C_3Ph_3)NiL]Y$ (Y = ClO_4, BPh_4). An uncharged derivative with the formula $[(C_3Ph_3)Ni(hb(3,5\text{-}me_2Pz)_3)]$ ($hb(3,5\text{-}me_2Pz)_3$ = hydrotris(3,5-dimethyl-1-pyrazolyl)borate) has also been prepared. The molecular structure of $[(C_3Ph_3)Ni(triphos)]ClO_4$ has been determined from counter diffraction data. The crystals are monoclinic, space group $P2_1/n$ with cell dimensions: a 17.750(5), b 17.629(5), c 16.509(4) Å; β 92.59(9)°, D_c = 1.359 g cm^{-3} for Z = 4. Full matrix least-squares refinement led to the conventional R factor of 0.064 for 2556 observed reflections. The molecular structure consists of $[(C_3Ph_3)Ni(triphos)]^+$ cations and ClO_4^- anions. The nickel atom is coordinated to the three phosphorus atoms of the triphos ligand, and to the C_3Ph_3 fragment in a symmetric η^3 fashion.

Introduction

Only a few organometallic complexes containing a cyclopropenyl group (C_3Ph_3) symmetrically η^3-bonded to the metal have been synthesized and fully characterized [1—3]. These are generally obtained as uncharged species by reaction of triphenylcyclopropenyl salts with metal carbonyls.

We have now found that reaction of the recently synthesized $[(C_3Ph_3)Ni(PPh_3)_2]ClO_4$ (I) [4] with tridentate ligands having N, P, or As donor atoms generates stable cationic complexes containing a coordinated η^3-C_3Ph_3 group. They have the general formula $[(C_3Ph_3)NiL]Y$ (L = 1,1,1-tris(dimethylphosphino-

0022—328X/81/0000—0000/$02.50, © 1981, Elsevier Sequoia S.A.

TABLE 1

ANALYTICAL AND ^{13}C NMR DATA FOR THE COMPLEXES

Compound	Found (calcd.) (%)						δ $^{13}C_3$ [a]
	C	H	Ni	N	As	P	
$(C_3Ph_3)Ni(hb(3,5\text{-}me_2Pz)_3$	69.31 (69.36)	5.90 (5.98)	8.90 (9.47)	13.47 (13.48)			54.4 A
$[(C_3Ph_3)Ni(metriphos)]BPh_4 \cdot \frac{1}{2}\ CH_2Cl_2$	72.80 (72.26)	6.92 (6.76)	6.37 (6.25)				54.6 B q (7)
$[(C_3Ph_3)Ni(triars)]ClO_4$	62.14 (62.99)	4.47 (4.57)	5.00 (4.97)		19.58 (19.03)		61.86 A
$[(C_3Ph_3)Ni(pnp)]BPh_4 \cdot CH_2Cl_2$	75.01 (76.24)	5.98 (5.24)	4.45 (4.84)	1.28 (1.15)		5.49 (5.11)	62.7 B (?)
$[(C_3Ph_3)Ni(triphos)]ClO_4$	69.68 (70.90)	5.11 (5.14)	5.75 (5.58)				62.7 A q (6)
$[(C_3Ph_3)Ni(ppp)]BPh_4$	80.44 (80.46)	5.93 (5.76)	5.30 (4.98)				63.41 B q (6)

[a] ^{13}C chemical shifts of the cyclopropenyl carbon atoms in ppm downfield from TMS, ±0.1 ppm; deuterochloroform (A) or deuteromethylene chloride (B) solutions; q = quartet; $^2J(^{13}P—M—^{13}C)$ coupling constants in Hz, ±0.5 Hz.

TABLE 2

POSITIONAL AND THERMAL PARAMETERS FOR $[(\eta^3\text{-}C_3Ph_3)Ni(triphos)]ClO_4$ [a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	2063(1)	2032(1)	4471(1)	407(9)	322(9)	388(9)	21(8)	42(7)	—16(8)
P(1)	1441(2)	3012(2)	3806(2)	453(20)	378(20)	443(21)	29(17)	38(16)	—18(17)
P(2)	3069(2)	2842(2)	4756(2)	446(19)	379(21)	463(20)	—31(17)	15(16)	—31(17)
P(3)	2578(2)	1630(2)	3292(2)	449(21)	409(20)	410(21)	13(17)	96(16)	—19(17)
Cl(1)	2857(2)	2639(2)	244(3)	817(30)	653(28)	846(31)	105(23)	64(27)	28(25)
O(2)	3377(5)	2115(6)	564(6)	949(73)	869(75)	1415(89)	399(73)	131(66)	301(67)
O(3)	2284(6)	2799(6)	804(7)	947(77)	1293(100)	1214(91)	374(78)	113(74)	—397(72)
O(4)	3261(7)	3297(6)	74(8)	1548(111)	666(67)	2528(147)	—112(85)	350(100)	707(73)
O(1)	2493(6)	2364(7)	—464(6)	1312(94)	2316(140)	834(76)	82(85)	—257(72)	—666(90)

[a] The form of the thermal ellipsoid is $\exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2\ U_{12}hka^*b^* + 2\ U_{13}hla^*b^* + 2\ U_{23}klb^*c^*))$. All quantities are multiplied by 10^4.

methyl)ethane, $CH_3C(CH_2P(CH_3)_2)_3$ (metriphos); 1,1,1-tris(diphenylphosphinomethyl)ethane, $CH_3C(CH_2P(C_6H_5)_2)_3$ (triphos); (bis(2-diphenylphosphino)-ethyl)phenylphosphine, $P(C_2H_4P(C_6H_5)_2)_2$ (ppp); bis(2-diphenylphosphinoethyl)-n-propylamine, $(1\text{-}C_3H_7)N(C_2H_4P(C_6H_5)_2)_2$ (pnp); 1,1,1-tris(diphenylarsinomethyl)ethane, $CH_3C(CH_2As(C_6H_5)_2)_3$ (triars); Y = ClO_4, BPh_4).

With the ligand hydrotris(3,5-dimethyl-1-pyrazolyl)borate (hb(3,5-$me_2Pz)_3$), an uncharged derivative with the formula $[(C_3Ph_3)Ni(hb(3,5\text{-}me_2Pz)_3)]$ has also been prepared.

The title complexes have been characterized and their physical properties studied by the usual methods. A complete X-ray structure determination has been performed for the compound $[(C_3Ph_3)Ni(triphos)]ClO_4$.

Experimental

Triphenylcyclopropenium perchlorate [5], triphos [6], triars [7], pnp [8], hb(3,5-$me_2Pz)_3$ [9] and I [4] were prepared by the methods previously described; metriphos was prepared by a method analogous to that used for the ligand 1,1,1-tris(diethylphosphinomethyl)ethane [10]; the ligand ppp was purchased from Strem Chemicals Inc., Danvers, Mass, and used without further purification. All other chemicals were reagent grade. All the reactions were carried out under nitrogen, using deoxygenated solvents.

Carbon-13 NMR spectra were taken in deuterochloroform or deuteromethylene chloride solutions and recorded at 20 MHz on a CFT 20 Varian spectrometer operating in the pulse Fourier-transform mode with proton noise decoupling and a deuterium lock.

Analytical and ^{13}C NMR data for the complexes prepared are given in Table 1.

Preparation of $[(C_3Ph_3)NiL]ClO_4$ (L = metriphos, triphos, ppp, pnp, triars)

The appropriate ligand (1 mmol) in 15 ml of tetrahydrofuran was added at room temperature to a solution of I (1 mmol) in tetrahydrofuran (20 ml). Butanol (20 ml) was added and a fast stream of nitrogen was passed through the solution until crystallization began. The crystals were filtered off, washed with butanol and light petroleum and dried in a stream of dry nitrogen. The tetraphenylborate derivatives were obtained by adding solid $NaBPh_4$ to solutions containing the perchlorate compounds. The crude products were recrystallized from methylene chloride/butanol.

Preparation of $[(C_3Ph_3)Ni(hb(3,5\text{-}me_2Pz)_3)]$

Potassium hydrotris(3,5-dimethyl-1-pirazolyl)borate (1 mmol) in methanol (10 ml) was added to a solution of I (1 mmol) in tetrahydrofuran (20 ml). After removal of the precipitated white powder, 1-butanol (10 ml) was added, and a brisk current of nitrogen passed through the solution until crystallization commenced. The crystals were separated by the method described above. The compound can be recrystallized from benzene/1-butanol.

Crystal data and data collection

The crystals of the compound $[(triphos)Ni(C_3Ph_3)]ClO_4$ are monoclinic, space group $p2_1/n$. Four units, formula $C_{62}H_{54}ClO_4P_3$, are contained in the unit cell

TABLE 3

THERMAL AND DERIVED POSITIONAL PARAMETERS OF GROUP ATOMS [a]

Atom	x	y	z	U (Å^2)
C(1)	1348(6)	1202(6)	4823(6)	351(29)
C(2)	1500(6)	1723(6)	5447(7)	452(33)
C(3)	2042(6)	1161(6)	5276(6)	344(29)
C(4)	1976(6)	3302(6)	2921(7)	433(33)
C(5)	3153(6)	3520(6)	3894(6)	427(32)
C(6)	3140(6)	2415(6)	2845(7)	477(33)
C(7)	2853(6)	3221(6)	3041(7)	475(34)
C(8)	3217(6)	3768(7)	2408(7)	556(36)
C(9)	474(4)	2946(4)	3357(3)	399(29)
C(10)	—111(4)	3077(4)	3875(3)	544(34)
C(11)	—859(4)	3001(4)	3590(3)	619(36)
C(12)	—1022(4)	2794(4)	2786(3)	680(39)
C(13)	—437(4)	2663(4)	2267(3)	654(39)
C(14)	311(4)	2739(4)	2552(3)	491(34)
C(15)	1347(4)	3877(5)	4404(4)	464(32)
C(16)	1248(4)	4577(5)	4026(4)	731(42)
C(17)	1129(4)	5222(5)	4490(4)	834(45)
C(18)	1110(4)	5166(5)	5331(4)	890(48)
C(19)	1209(4)	4466(5)	5709(4)	789(45)
C(20)	1327(4)	3821(5)	5246(4)	538(35)
C(21)	4033(4)	2461(4)	4860(4)	465(32)
C(22)	4133(4)	1679(4)	4835(4)	495(34)
C(23)	4859(4)	1375(4)	4871(4)	712(41)
C(24)	5485(4)	1852(4)	4932(4)	681(40)
C(25)	5385(4)	2633(4)	4957(4)	715(41)
C(26)	4659(4)	2938(4)	4921(4)	671(38)
C(27)	3092(4)	3505(4)	5617(5)	498(34)
C(28)	2830(4)	3231(4)	6345(5)	657(41)
C(29)	2818(4)	3702(4)	7022(5)	769(42)
C(30)	3068(4)	4447(4)	6971(5)	796(43)
C(31)	3330(4)	4721(4)	6243(5)	902(49)
C(32)	3342(4)	4250(4)	5566(5)	764(44)
C(33)	1952(4)	1300(4)	2435(4)	442(31)
C(34)	1184(4)	1187(4)	2535(4)	496(33)
C(35)	731(4)	883(4)	1904(4)	606(37)
C(36)	1046(4)	691(4)	1173(4)	662(39)
C(37)	1814(4)	803(4)	1073(4)	674(39)
C(38)	2267(4)	1108(4)	1704(4)	575(36)
C(39)	3241(3)	839(5)	3307(4)	397(31)
C(40)	3043(3)	188(5)	3725(4)	491(33)
C(41)	3532(3)	—429(5)	3765(4)	650(39)
C(42)	4219(3)	—396(5)	3388(4)	635(39)
C(43)	4416(3)	255(5)	2970(4)	676(39)
C(44)	3927(3)	872(5)	2930(4)	598(37)
C(45)	726(3)	783(4)	4413(4)	389(30)
C(46)	836(3)	47(4)	4141(4)	500(34)
C(47)	248(3)	—338(4)	3730(4)	561(37)
C(48)	—449(3)	14(4)	3591(4)	580(36)
C(49)	—559(3)	751(4)	3863(4)	573(37)
C(50)	29(3)	1135(4)	4274(4)	466(32)
C(51)	1131(3)	2020(4)	6172(5)	438(30)
C(52)	1501(3)	1966(4)	6933(5)	584(35)
C(53)	1152(3)	2229(4)	7619(5)	755(42)
C(54)	432(3)	2545(4)	7544(5)	811(45)
C(55)	62(3)	2599(4)	6783(5)	713(41)
C(56)	411(3)	2336(4)	6097(5)	551(35)
C(57)	2552(4)	638(3)	5714(5)	382(30)
C(58)	3109(4)	926(3)	6253(5)	511(35)
C(59)	3585(4)	434(3)	6694(5)	624(58)
C(60)	3505(4)	—345(3)	6596(5)	683(40)
C(61)	2948(4)	—633(3)	6057(5)	549(34)
C(62)	2472(4)	—141(3)	5617(5)	493(33)

[a] All quantities are multiplied by 10^4.

which has dimensions: a 16.750(5), b 17.629(5), c 16.509(4) Å, β 92.59(9)°. The crystal chosen for data collection was a polyhedron with faces of the forms {011}, {101} and {$\bar{1}$01} and maximum dimensions along crystal axes 0.18 × 0 × 18 × 0.15 mm. Intensity data were collected on an automatic computer-controlled Philips Pw 1100 diffractometer, equipped with a graphite monochromater, using Mo-k_α radiation. The θ—2 θ scan technique was employed with a scan range of 0.80° in θ, at a scan rate of 0.05° s^{-1}. The background measurement time at each side of the scan was determined as (scan time)/2. 4853 unique reflections were measured up to θ = 20°, 2556 of which were considered observed having $I \geqslant 3\ \sigma\ (I)$. An absorption correction μ(Mo-K_α) = 5.28 was applied by a numerical method: transmission factors varied between 0.88 and 0.96.

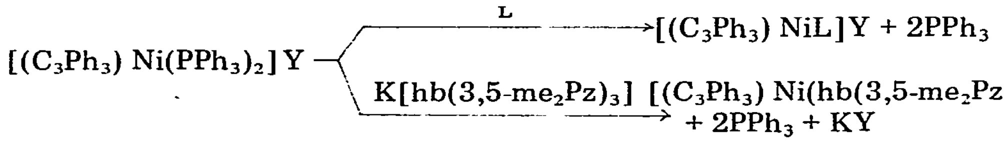
Structure determination and refinement

Computation was carried out on a SEL 32/70 computer using a selection of programs from SHELX-76 [11], XRAY-76 [12] and a locally written set.

The structure was solved by direct methods. Full-matrix least-squares refinement was initiated after a number of F_0 and ΔF maps had enabled us to determine the positions of all the non-hydrogen atoms. Throughout the refinement all the phenyl groups were treated as rigid bodies with D_{6h} symmetry and C—C distances of 1.395 Å. After two cycles using an isotropic thermal model for all the atoms, the R factors ($R = \Sigma |F|/\Sigma |F_c|$) dropped to 0.12. The minimized function was $\Sigma w(|F_0| - |F_c|)^2$ where w is the weight assigned to the F_0 values according to the expression $w = 1/\sigma^2(F_C)$. Subsequently, hydrogen atoms were introduced at the calculated positions (C—H distances of 0.95 Å). Anisotropic temperature factors were used for Ni, P, Cl, and O species. The final refinement gave an R value of 0.064 and R_w of 0.060. A final ΔF Fourier synthesis did not show any noteworthy features, except for some disorder in the perchlorate region, as expected considering the high thermal motion of the oxygen atoms. The final position and thermal parameters are reported in Table 2. Tables of structure factors are available from the authors.

Results and discussion

The complex [(C_3Ph_3)Ni(PPh_3)$_2$]ClO_4 reacts rapidly at room temperature with the tridentate ligands metriphos, triphos, ppp, pnp, triars and hb(3,5-me$_2$Pz) according to the reaction scheme below to form the complexes [(C_3Ph_3)NiL]Y



$$[(C_3Ph_3)\,Ni(PPh_3)_2]Y \begin{cases} \xrightarrow{L} [(C_3Ph_3)\,NiL]Y + 2PPh_3 \\ \xrightarrow{K[hb(3,5\text{-}me_2Pz)_3]} [(C_3Ph_3)\,Ni(hb(3,5\text{-}me_2Pz)_3] + 2PPh_3 + KY \end{cases}$$

(L = metriphos, triphos, ppp, pnp, triars; Y = ClO_4, BPh_4) and [(C_3Ph_3)Ni(hb(3,5-me$_2$Pz)$_3$)]. All the crystalline complexes are diamagnetic and air stable, and decompose very slowly in solution in chlorinated solvents; the phosphino and arsino derivatives are 1 : 1 electrolytes in nitroethane solution.

The molecular structure of the compound [(C_3Ph_3)Ni(triphos)]ClO_4 consists of [(C_3Ph_3)Ni(triphos)]$^+$ cations (Fig. 1) and ClO_4^- anions. The nickel atom is coordinated to the three phosphorus atoms of the triphos ligand and to the

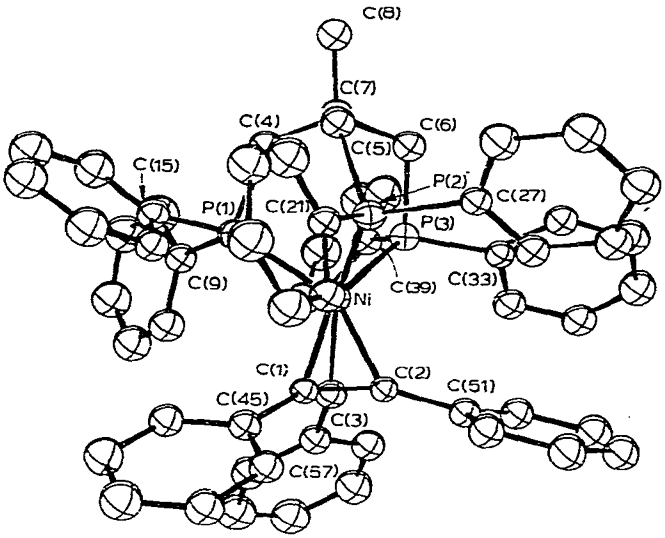


Fig. 1. Perspective view of the $[(\eta^3\text{-}C_3Ph_3)Ni(triphos)]^+$ cation.

C_3Ph_3 fragment in a symmetric η^3 fashion. The molecule possesses non-crystallographic C_{3v} symmetry; the orientation of the triphos ligand being staggered with respect to the cyclopropenyl ring. Bond distances and angles (Table 4) within (triphos)Ni compare well with those found in a variety of compounds containing this moiety [13]. The C—C bonds, both in the three-membered ring (1.41(1) Å average) and those connecting this ring with the phenyl groups (1.47(1) Å average), compare well with the analogous distances reported for structures such as $[(C_3Ph_3)Ni(C_5H_5)$ [2], $[(C_3Ph_3)Co(CO_3]$ [3] and others quoted in reference 13. The Ni—C (C_3Ph_3) bond distances in the present compound (2.030(3) Å) are somewhat longer than in the other two complexes which con-

TABLE 4

SELECTED BOND LENGTHS (Å) AND ANGLES (deg)

Ni—P(1)	2.308(3)	C(2)—C(51)	1.486(13)
Ni—P(2)	2.322(3)	C(3)—C(57)	1.464(12)
Ni—P(3)	2.301(3)	P(1)—C(4)	1.851(11)
Ni—C(1)	2.043(10)	P(2)—C(5)	1.872(11)
Ni—C(2)	2.010(11)	P(3)—C(6)	1.881(12)
Ni—C(3)	2.036(10)	C(4)—C(7)	1.567(15)
C(1)—C(2)	1.401(15)	C(5)—C(7)	1.575(15)
C(1)—C(3)	1.412(14)	C(6)—C(7)	1.554(16)
C(2)—C(3)	1.421(15)	C(7)—C(8)	1.584(16)
C(1)—C(45)	1.470(12)		
P(1)—Ni—P(2)	88.82(12)	C(1)—C(1)—C(3)	60.7(7)
P(1)—Ni—P(3)	91.71(11)	C(1)—C(2)—C(3)	60.1(7)
P(2)—Ni—P(3)	91.77(12)	C(1)—C(3)—C(2)	59.2(7)
C(1)—Ni—C(2)	40.4(4)	Ni—C(1)—C(45)	134.0(7)
C(1)—Ni—C(3)	40.5(4)	Ni—C(2)—C(51)	143.4(7)
C(2)—Ni—C(3)	41.1(4)	Ni—C(3)—C(57)	140.6(7)

other P—C distances (average) 1.848(14)
Cl—O (average) 1.407(18)

tain a Ni—$(C_3Ph_3)\eta^3$ linkage i.e. $[(C_3Ph_3)NiCl(py)_2]$ [1] and $[(C_3Ph_3)Ni(C_5H_5)]$ [2] with average Ni—C distances of 1.941(5) and 1.961(4) Å, respectively.

A different distribution of residual charges in our cationic compound with respect to the above uncharged species may be important in causing these geometrical differences. However, the steric repulsions exerted by the bulky phenyl rings of the triphos ligand on the phenyl rings of the C_3Ph_3 fragment are also import in lengthening the Ni—C distances. Such a steric effect is also evident from the value of the tilt angles (defined as the angles between the plane of the C_3 ring and the C—C (Ph) bonds), which in the present case (20.1°, 30.3° and 26.7°) are all larger than in an ideal tetrahedral molecule (19.47°) and in the other Ni—C_3Ph_3 fragments (20.1°, 19.2, 19.7° in $(C_3Ph_3)Ni(C_5H_5)$).

The ^{13}C NMR spectra of the compounds show resonances for the cyclopropenyl carbon atoms at δ 54.4—63.41 ppm (Table 1) which are consistent with a three-fold symmetry of the C_3Ph_3 group in all the complexes. These values are very similar to those previously reported for the $[(\eta_3\text{-}C_3Ph_3)Ni(C_5H_5)]$ and $[(C_3Ph_3)Co(CO)_3]$ compounds [3].

If we now consider the moieties $[Ni(triphos)]^+$, $[Ni(metriphos)]^+$ etc. as isolobal with the fragments $Co(CO)_3$ and $Ni(C_5H_5)$, the MO approach recently developed by Hoffmann and al. [14] for the bonding of the latter fragments to cyclopropenium can be used. Thus even in our case the high energy $2a_1$ and $2e$ orbitals match perfectly with the a_2'' and e'' orbitals of C_3Ph_3 only in a η^3 bonding scheme.

Acknowledgements

The authors thank Mr. F. Cecconi for technical assistance, Mr. P. Innocenti for NMR measurements, and Mr. G. Vignozzi and Mr. F. Nuzzi for microanalyses.

References

1 R.M. Tuggle and D.L. Weaver, Inorg. Chem., 10 (1971) 1504.
2 R.M. Tuggle and D.L. Weaver, Inorg. Chem., 10 (1971) 2599.
3 T. Chiang, R.C. Kerber, S.D. Kimball and J.W. Lauher, Inorg. Chem., 18 (1979) 1687.
4 C. Mealli, S. Midollini, S. Moneti and L. Sacconi, Angew. Chem., in press.
5 R. Breslow and H.W. Chang, J. Amer. Chem. Soc., 83 (1961) 2374.
6 W. Hewertson and M.R. Watson, J. Chem. Soc., (1962) 1490.
7 S. Midollini, F. Cecconi, J. Chem. Soc., Dalton Trans., (1973) 681.
8 P. Dapporto, R. Morassi and L. Sacconi, J. Chem. Soc. A., (1969) 1298.
9 J.P. Jessow, S. Trofimenko and D.R. Eaton, J. Amer. Chem. Soc., 89 (1967) 3148.
10 C. Bianchini, A. Meli, A. Orlandini and L. Sacconi, submitted for publication.
11 'SHELX-76' System of Programs, G.M. Sheldrick (1976).
12 'XRAY-76' System of Programs, J.M. Stewart, Computer Science Center, University of Maryland (1976).
13 F. Mani and L. Sacconi, Transition Metal Chem., in press.
14 E.D. Jemmis, R. Hoffmann, J. Amer. Chem. Soc., 102 (1980) 2570.