221. Transition Metal Complexes with Bidentate Ligands Spanning *trans*-Positions. VIII[1]). The Reactions of the Nucleophile *trans*-[RuCl(NO)(1)] (1 = 2,11-Bis(diphenylphosphinomethyl)benzo[*c*]-phenanthrene) with Carbon Monoxide and the Phosphite Ligand (2) (2 = 1-Ethyl-3,5,8-trioxa-4-phosphabicyclo(2.2.2)octane)

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Summary

The preparation of the nucleophile *trans*-[RuCl(NO)(**1**)], where **1** is the bidentate ligand $Ph_2PCH_2C_{18}H_{10}CH_2PPh_2$, and of the five-coordinate species [RuCl(CO)(NO)(**1**)], [RuCl(CO)(NO)$(Ph_2PCH_2Ph)_2$] and [RuCl(NO)(**2**)(**1**)] are reported.

The crystal structure of [RuCl(CO)(NO)(**1**)] shows that the coordination around the metal atom is distorted trigonal bipyramidal with the phosphorus atoms in axial positions. The Ru–N–O bond angle is 142.8°. ^{1}H- and ^{31}P-NMR. and $\tilde{\nu}_{NO}$ IR.-data for the above complexes are reported and related to the coordination geometry.

1. Introduction. - Ligand addition reactions in complexes of the type *trans*-[IrX(CO)(**1**)] (**3a**), occur less easily [2] than in the corresponding complexes with monodentate phosphines [3]. Thus, complexes [IrX(CO)(L)(**1**)] (L = CO, SO_2) could only be detected in solution.

As *trans*-[RuCl(NO)$(PPh_3)_2$] shows a marked tendency towards addition of a fifth ligand [4] the complex *trans*-[RuCl(NO)(**1**)] (**3b**) was prepared and its reactions with carbon monoxide and the phosphite **2** studied.

2. Results and Discussion. - 2.1. *Preparation of the complexes.* - The complex **3b** was prepared by phosphine exchange from *trans*-[RuCl(NO)$(PPh_3)_2$] [4]. For comparison purposes *trans*-[RuCl(NO)$(Ph_2PCH_2Ph)_2$] (**4**), was also prepared as described by *Stiddard & Townsend* [4] for its triphenylphosphine analogue. A

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[1]) Part VII: see [1].

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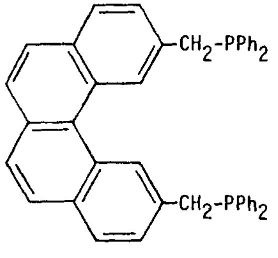

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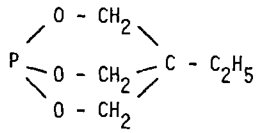

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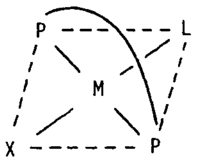

3a M=Ir; L=CO; X=Cl,Br,J
3b M=Ru; L=NO; X=Cl

suspension of **3b** in benzene reacted readily with carbon monoxide giving [RuCl(CO)(NO)(**1**)] (**5**). The complex [RuCl(CO)(NO)($Ph_2PCH_2Ph)_2$] (**6**) was similarly prepared. The complex [RuCl(NO)(**2**)(**1**)] (**7**) was prepared by addition of the phosphite **2** to **3b**. IR. and NMR. spectral parameters are shown in *Table 1.*

Complexes of this type are expected to have distorted square pyramidal structures as found in the related [IrX(CO)(NO)($PPh_3)_2$][BF_4] (X=Cl and I) [5] [6] and [RuCl($NO)_2$($PPh_3)_2$][PF_6] [7]. The crystal structure of [RuI(CO)(NO)($PPh_3)_2$] [8] has been determined but the extent of the deviation from regular geometry could not be established because of disorder between the CO and NO ligands. In order to assess the influence of a ligand such as **1** on the coordination polyhedron in these five-coordinate species, the crystal structure of **5** was determined.

Table 1. *NMR. and IR. spectral parameters for ruthenium nitrosyl complexes*

	^{31}P-NMR.	^{1}H-NMR.			IR.		
	$\delta(^{31}P)$ [ppm][a])	$\delta(CH_2)$ [ppm]	$^2J_{H,H}$ [Hz]	$\lvert ^2J_{P,H}+{}^4J_{P,H}\rvert$ [Hz]	$\tilde{\nu}_{NO}$ [cm^{-1}]	$\tilde{\nu}_{NO}$(corr.)[b]) [cm^{-1}]	$\tilde{\nu}_{CO}$ [cm^{-1}]
[RuCl(NO)($PPh_3)_2$]	31.8				1762[c])	1782	
[RuCl(NO)($Ph_2PCH_2Ph)_2$] (**4**)	33.1	4.21[d])		8.1[e])	1740[f])	1760	
[RuCl(NO)(**1**)] (**3b**)	31.5	5.10 4.14[g])	13.8	7.3 11.3	1720[h])	1740	
[RuCl(NO)(CO)($PPh_3)_2$]	33.7				1595[i])	1565	1925
[RuCl(NO)(CO)($Ph_2PCH_2Ph)_2$] (**6**)	35.1	4.75 3.78[d])	13.2	8.6 10.6	1605[j])	1575	1920
[RuCl(NO)(CO)(**1**)] (**5**)	36.7	5.17 3.88[g])	14.2	9.5 11.6	1672[h])	1642	1915
[RuCl(NO)(**2**)(**1**)] (**7**)	36.3*d*[k]) 142.2*t*	6.10 3.64[d])	13.8	10.1 11.0	1654[h])	1624	

[a]) Relative to H_3PO_4 with a positive value indicating a shift to lower field. All spectra in C_6D_6-solution. [b]) See [21]. [c]) See [9]. [d]) C_6D_6 solutions. [e]) Pseudo-triplet. [f]) C_6H_6 solution, 0.1 mm path. [g]) CD_2Cl_2 solutions. [h]) Nujol mull. [i]) See [20]. [j]) KBr disk. [k]) *d* = doublet, *t* = triplet, $^2J_{P,P}$ = 44.1 Hz, measured in C_6D_6.

2.2. *Crystal Structure of [RuCl(CO)(NO)*(**1**)*]*. The crystal consists of discrete molecules of **5** and disordered CD_2Cl_2. A perspective view of the complex is shown in the *Figure*. Important bond lengths and angles are given in *Table 2*. The coordination around the ruthenium atom is best described as a distorted trigonal bipyramid with the

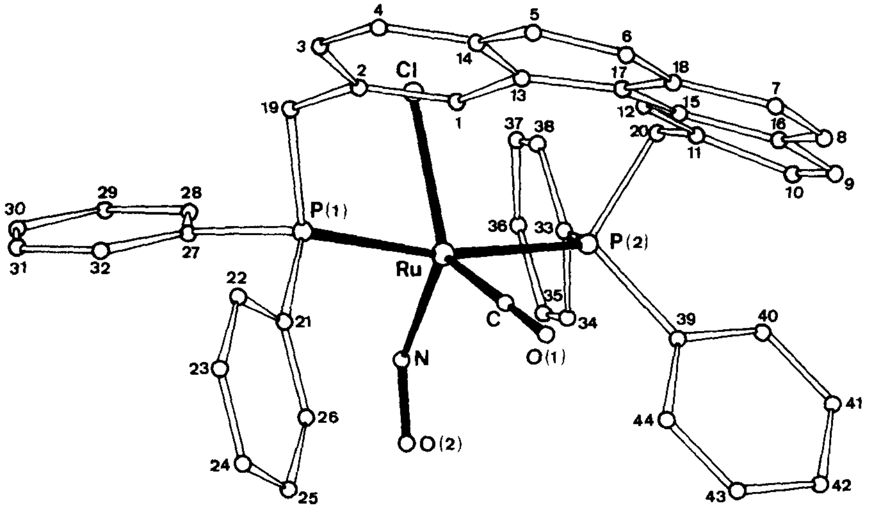

Figure. *Perspective view of the molecule [RuCl(CO)(NO)*(**1**)*]*

Table 2. *Selected bond lengths and angles in* **5**

Ru–P(1)	2.410(2) Å	P(1)–Ru–P(2)	167.4(1)°
Ru–P(2)	2.391(2)	P(1)–Ru–Cl	85.2(1)
Ru–Cl	2.486(2)	P(1)–Ru–C	90.2(3)
Ru–C	1.828(9)	P(1)–Ru–N	98.5(2)
Ru–N	1.839(7)	P(2)–Ru–Cl	84.88(1)
C–O(1)	1.146(11)	P(2)–Ru–C	91.3(3)
N–O(2)	1.173(8)	P(2)–Ru–N	93.0(2)
P(1)–C(19)	1.843(7)	Cl–Ru–C	134.6(2)
P(1)–C(21)	1.825(5)	Cl–Ru–N	119.1(2)
P(1)–C(27)	1.857(6)	C–Ru–N	106.3(3)
P(2)–C(20)	1.847(7)	Ru–C–O(1)	179.0(6)
P(2)–C(33)	1.846(6)	Ru–N–O(2)	142.8(7)
P(2)–C(39)	1.836(5)	Ru–P(1)–C(19)	115.3(3)
C(2)–C(19)	1.506(12)	Ru–P(1)–C(21)	116.2(2)
C(11)–C(20)	1.532(14)	Ru–P(1)–C(27)	114.2(2)
		C(19)–P(1)–C(21)	106.0(3)
		C(19)–P(1)–C(27)	99.9(3)
		C(21)–P(1)–C(27)	103.3(2)
		Ru–P(2)–C(20)	112.4(3)
		Ru–P(2)–C(33)	110.8(2)
		Ru–P(2)–C(39)	120.0(2)
		C(20)–P(2)–C(33)	105.3(4)
		C(20)–P(2)–C(39)	104.4(3)
		C(33)–P(2)–C(39)	102.5(3)
		C(2)–C(19)–P(1)	118.8(5)
		C(11)–C(20)–P(2)	112.3(5)

phosphorus atoms occupying axial positions. The metal centre, the chlorine atom, the CO and NO ligands are almost exactly coplanar. The plane through these six atoms can be taken as the equatorial plane of the bipyramid. The Ru–P(1) and Ru–P(2) bonds make angles of 81.1 (6) and 85.8 (2)° respectively with the equatorial plane. The distortion of the bipyramid is toward a square pyramid having the NO group at the apex. The Ru–N–O angle of 142.8(7)° indicates that the NO-ligand can be considered as NO^-, and hence ruthenium is assigned a formal oxidation state of +2. The formation of complex **5** may then be described as follows: addition of CO to the d^8-ruthenium(0) complex, [RuCl(NO)(**1**)], causes the intramolecular redox process Ru(0)–$NO^{(+)} \rightarrow$ Ru(II)–$NO^{(-)}$ [9], giving the five-coordinate, coordinatively unsaturated d^6-ruthenium complex [RuCl(CO)(NO)(**1**)]. It is interesting to compare the structural parameters of **5** with those of the related isoelectronic species $[RuCl(NO)_2(PPh_3)_2][PF_6]$ (**9**) [7] and $[IrCl(CO)(NO)(PPh_3)_2][BF_4]$ (**10**) [5]. Relevant bond lengths and angles are summarized in *Table 4.*

The most notable difference is the more nearly trigonal bipyramidal structure of the complex **5** containing ligand **1**. Examination of non-bonded contacts *(Table 3)* shows that a more nearly square pyramidal structure would not have resulted in greater steric interactions.

Another difference is in the Cl–M–X, Cl–M–N and X–M–N equatorial bond angles (X = the linear nitrosyl in **9** or CO in **5** and **10**. Changes in equatorial angles, *e.g.,* from **10** to **9** to **5**, are accompanied by changes in the M–N–O angle, *i.e.,* as the coordination changes from a square pyramid toward a trigonal bipyramid the M–N–O angle increases. This is in accordance with theoretical considerations involving symmetry arguments and Extended Hückel MO. calculations, which

Table 3. *Distances between non-bonded atoms in* **5**

Chlorine		Carbonyl				Nitrosyl			
Cl···C(19)	3.446 Å	C···C(1)	3.394 Å	O···C(1)	3.587 Å	N···C(26)	3.720 Å	O···C(26)	3.724 Å
Cl···C(20)	3.497	C···C(12)	3.381	O···C(12)	3.547	N···C(27)	3.725		
Cl···C(27)	3.885	C···C(20)	3.897			N···C(32)	3.615		
Cl···C(32)	3.541	C···C(21)	3.382	O···C(21)	3.719	N···C(33)	3.544		
Cl···C(33)	3.659	C···C(26)	3.364	O···C(26)	3.560	N···C(34)	3.696	O···C(34)	3.989
Cl···C(38)	3.408	C···C(39)	3.573	O···C(39)	3.962	N···C(39)	3.872		
		C···C(44)	3.279	O···C(44)	3.385	N···C(44)	3.813	O···C(44)	3.639

Table 4. *Comparison of the nitrosyl geometry in the coordination sphere of three isoelectronic pentacoordinate compounds*

	5	**9**[a])	**10**[b])
M–N–O	142.8°	138°	124.1
Cl–M–N	119.1	102.2	101.3
Cl–M–X[c])	134.6	155.8	161.3
N–M–X[c])	106.3	102	97.4
P–M–P	167.4	159.6	175.7

[a]) See [7]. [b]) See [5]. [c]) X is the nitrogen atom of the linear nitrosyl in **9** and the carbon atom of the carbonyl in **5** and **10**.

predict that 'the nitrosyl is less likely to bend in the equatorial position of a trigonal bipyramid than in the apical site of a square pyramid' [10]. The Ru–N bond length [1.839(7) Å] in **5** agrees with the apical Ru–N distance [1.85(2) Å] in $[RuCl(NO)_2(PPh_3)_2]^+$ [7] but is significantly longer than the bond to the basal NO group in the same complex, in agreement with the expectation that NO^- is a poor π-acceptor [5]. The N–O bond length in **5** [1.173(8) Å] is also consistent with a negatively charge on the nitrosyl ligand, which is bent toward the carbonyl group. A similar bending occurs toward the carbonyl group in $[IrX(CO)(NO)(PPh_3)_2]^+$ (X=Cl, I) [5] [6], and toward the linear NO^+ group in $[RuCl(NO)_2(PPh_3)_2]^+$ [7] and $[Os(OH)(NO)_2(PPh_3)_2]^+$ [11]. Theoretically nitrosyl should bend toward the ligand with greatest π-acceptor ability [10] because of the interaction between a filled lone pair orbital of the oxygen and an empty π^* orbital of CO or NO^+ [7].

The carbonyl group has Ru–C and C–O bond lengths of 1.828(9) and 1.146(11) Å respectively, and the Ru–C–O angle is 179.0(6)°. These values are comparable with those in $[Ru(OAc)(p\text{-}MeC_6H_4NCH)(CO)(Ph_3P)_2]$ [12].

The Ru,Cl-bond [2.486(2) Å] is much longer than in other pentacoordinate ruthenium(II) complexes {2.362(6) Å in $[RuCl(NO)_2(PPh_3)_2]^+$ [7], 2.387(7) and 2.388(7) Å in $[RuCl_2(PPh_3)_3]$ [13], 2.421(5) Å in $[RuHCl(PPh_3)_3]$ [14]}, but is similar to the bond (2.513(7) Å) *trans* to a phosphine in octahedral $[RuCl_3(EtPh_2P)_3]^-$ [15]. The length of the Ru,Cl-bond in **5** is in keeping with the low $\tilde{\nu}$(Ru–Cl) observed for the corresponding triphenylphosphine complex $[RuCl(CO)(NO)(PPh_3)_2]$ [16].

The Ru,P-bonds [average length 2.401(2) Å] fall in the range (2.37-2.43 Å) generally found for mutually *trans* Ru,P-bonds in penta-coordinate ruthenium(II) complexes [7] [14] [17].

The deviation of the P–Ru–P angle [167.4(1)°] from linearity as an expression of the distortion of the bipyramid toward a square pyramid. The P–M–P bond angles in some square-planar and octahedral complexes, in which ligand **1** spans *trans*-positions, are summarized in *Table 5*. Elongation of M–P and consequently of P···P is accompanied by decrease of the P–M–P bond angle.

The geometry of the 2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene ligand resembles that found in other complexes [18].

2.3. *IR. Data.* - The NO-stretching frequencies are generally indicative of the type of bonding in metal nitrosyl complexes. Thus, empirical rules have been derived [21] to distinguish between a formally NO^+ from a formally NO^- coordinated group. The NO-stretching frequencies *(Table 1)* of the four-coordinate

Table 5. *Geometry of the 'linear' P–M–P moiety in some complexes of ligand* **1**

	M–P[a])	P–M–P	P···P
trans-$[PdCl_2(\mathbf{1})]$[b])	2.324 Å	175.7°	4.645 Å
trans-$[RhCl(CO)(\mathbf{1})]$[b])	2.315	174.7	4.624
trans-$[PtHCl(\mathbf{1})]$[c])	2.280	176.2	4.558
$[IrCl_3(CO)(\mathbf{1})]$[d])	2.411	170.7	4.805

[a]) Average value. [b]) See [2]. [c]) See [19]. [d]) See *F.J.S. Reed, E. Baumgartner, R. Holderegger, L.M. Venanzi, F. Bachechi, L. Zambonelli,* to be published.

complexes [RuCl(NO)L$_2$] (L = Ph$_3$P, Ph$_2$PCH$_2$Ph; L$_2$ = **1**) fall in the range where the nitrosyl is described as NO$^+$ [21]. The slight differences probably reflect the influence of differences in donor properties of the phosphines and/or minor structural changes.

The NO-stretching frequencies of the five-coordinate complexes are also listed in *Table 1*. The NO-frequency and the Ru–N–O bond angle in **5** (1672 cm^{-1} and 143° respectively) do not fit the generalisation proposed by *Haymore & Ibers* [21] according to which linear and bent nitrosyl groups show 'corrected' NO-bands respectively above and below 1610-1620 cm^{-1}. The other exception [IrI(CO)(NO)(Ph$_3$P)$_2$][BF$_4$] [21] is formally 'iso-electronic' with **5** and has an Ir–N–O bond angle of 125° and $\tilde{\nu}_{NO}$(corr.) = 1640 cm^{-1}. According to the criterion of *Haymore & Ibers* [21] the complexes [RuCl(CO)(NO)L$_2$] (L = Ph$_3$P and Ph$_2$PCH$_2$Ph) should have bent Ru–N–O groups. The absorption bands *(Table 1)* indicate microsymmetries similar to those in [IrX(CO)(NO)(Ph$_3$P)$_2$][BF$_4$] (X = Cl, I) [5] [6], *i.e.*, approaching square pyramidal coordination with Ir–N–O bond angles of *ca.* 125°. The postulated formal change in oxidation state on addition of a fifth ligand is supported by the change in $\tilde{\nu}_{NO}$ that occurs when CO or phosphite **2** is added to four-coordinate complexes. A lowering of *ca.* 150 cm^{-1} is observed for [RuCl(CO)(NO)L$_2$] (L = Ph$_3$P and Ph$_2$PCH$_2$Ph) and of 50 cm^{-1} for the corresponding complex with ligand **1**.

The NO-band found for **7** is similar to that of **5**, and it is presumed that the two complexes have similar structures.

2.4. *NMR. Data.* - ^{1}H-NMR. spectra are similar to those of related complexes [2]. Thus the CH$_2$-protons in complexes of ligand **1** give a set of four triplets which have been assigned to the spin-system *AMXX'M'A'*. Reasons for the appearance of this type of spectrum have been discussed elsewhere [2].

The CH$_2$-protons in [RuCl(CO)(NO)(Ph$_2$PCH$_2$Ph)$_2$] also give four triplets assigned to the same spin system. Similar spectra have been reported for complexes of Pd(II) containing phosphines with benzylic substituents [22].

^{31}P-NMR. chemical shifts *(Table 1)* for the four five-coordinate species examined are very similar and do not reflect the structural changes indicated by the IR. spectra. The spectrum of **7** shows the expected low-field resonance due to the phosphite ligand [23] coupled to the phosphorus atoms of ligand **1**.

3. Experimental Part. - 3.1. *Generalities and Physical Measurements.* See [1].

3.2. *Preparation of the complexes.* All reactions were carried out under nitrogen.

3.2.1. *[RuCl$_3$(NO)(PPh$_3$)$_2$].* The solution of 600 mg NaNO$_2$ in 10 ml water was added slowly to a refluxing stirred solution of 1 g RuCl$_3$ · xH$_2$O in 10 ml 1.0M HCl. After 10 min the wine-red solution was evaporated to dryness and the solid extracted with 20 ml ethanol. This extract was added dropwise to a hot ethanol solution of 2.528 g PPh$_3$. After cooling, the precipitate was filtered off and washed with 20 ml of a ethanol/dichloromethane/hexane 1:1:2 and dried i.V. The brownish yellow product shows a single resonance in the ^{31}P-NMR. spectrum at 24.42 ppm (C$_6$D$_6$). Yield: 50%.

3.2.2. *[RuCl(NO)(***1***)]* (**3b**). The solution of 228 mg (0.3 mmol) [RuCl$_3$(NO)(PPh$_3$)$_2$] and 1 g Zn-dust in 25 ml benzene were stirred refluxing for 2 h. The green solution was filtered and evaporated to 5 ml. 206 mg (0.33 mmol) of ligand **1** was added and the slurry stirred for 20 h. The green precipitate was filtered off and dried i.V. Yield: 86%.

C$_{44}$H$_{34}$ClNOP$_2$Ru	Calc.	C 66.85	H 4.34	N 1.77	P 7.83%	(M.W. 791.23)
	Found	„ 66.07	„ 4.36	„ 1.61	„ 6.90%	

3.2.3. *[RuCl(NO)(CO)(**1**)]* (**5**). Starting from 556 mg (0.6 mmol) [$RuCl_3(NO)(PPh_3)_2$] the compound [RuCl(NO)(**1**)] (**3b**) was prepared as described above. A slurry of the product in 20 ml benzene was stirred and a stream of CO was passed through it for 5 min. The light-brown solution so produced was concentrated and the product precipitated with light petroleum (b.p. 30-60°). Brown solid of dec.p. 200-210°. Yield: 55%.

$C_{45}H_{34}ClNO_2P_2Ru$	Calc.	C 65.98	H 4.18	N 1.71	P 7.56%	(M.W. 819.24)
	Found	„ 65.36	„ 4.39	„ 1.70	„ 7.64%	(M.W. 793)

3.2.4. *[RuCl(NO)(**2**)(**1**)]* · C_6H_6 (**7**). Compound [RuCl(NO)(**1**)] (**3b**) was prepared as described above starting from 342 mg (0.45 mmol) [$RuCl_3(NO)(PPh_3)_2$]. To a slurry of the product in 20 ml benzene 73 mg (0.45 mmol) of **2** dissolved in 5 ml benzene was added. After 30 min the red solution was concentrated and the product precipitated with light petroleum/ethanol 10:1. Yellowish brown product of dec.p. 150°. Yield: 44%.

$C_{56}H_{51}ClNO_4P_3Ru$	Calc.	C 65.21	H 4.98	N 1.35%	(M.W. 1031.47)
	Found	„ 65.05	„ 4.95	„ 1.39%	

3.2.5. *[$RuCl_3(NO)(Ph_2PCH_2Ph)_2$]*. This complex was prepared as described for [$RuCl_3(NO)(PPh_3)_2$]. Yellow product of dec.p. 220°. Yield: 68%. This compounds has a $\tilde{\nu}_{NO}$ at 1855 cm^{-1} (Nuyol mull). The ^1H-NMR. spectrum shows for the CH_2-groups a triplet at 4.40 ppm ($CDCl_3$ solution) with a coupling constant $|^2J_{P,H}+{}^4J_{P,H}|$ of 8.8 Hz. In the ^{31}P-NMR. a single resonance at 19.62 ppm ($CDCl_3$ solution) is observed.

$C_{38}H_{34}Cl_3NOP_2Ru$	Calc.	C 57.77	H 4.34	N 1.77	P 7.84%	(M.W. 790.06)
	Found	„ 57.49	„ 4.63	„ 2.06	„ 7.45%	(M.W. 784)

3.2.6. *[$RuCl(NO)(Ph_2PCH_2Ph)_2$]* (**4**). This complex was prepared by reduction of [$RuCl_3(NO)(Ph_2PCH_2Ph)_2$] with Zn-dust, but due to its sensitivity, the compound was not isolated. The spectral data in *Table 1* were measured with samples from the reaction mixture.

3.2.7. *[$RuCl(NO)(CO)(Ph_2PCH_2Ph)_2$]* (**6**). The solution of 300 mg (0.38 mmol) [$RuCl_3(NO)(Ph_2PCH_2Ph)_2$] in 30 ml benzene was reduced to **4** as above. The green solution so produced was filtered and then a stream of CO was passed through it. The colour changed immediately to brown. After concentrating to 3 ml the product was precipitated with light petroleum/hexane 1:1. Brown product of dec.p. 155-160°. Yield: 55%.

$C_{39}H_{34}ClNO_2P_2Ru$	Calc.	C 62.69	H 4.58	N 1.87	P 8.39%	(M.W. 747.17)
	Found	„ 61.99	„ 4.58	„ 2.08	„ 7.97%	

3.3. *Crystal Data.* Brown red crystals of [RuCl(NO)(CO)(**1**)] were obtained by slow evaporation of a CD_2Cl_2 solution. One disordered molecule of CD_2Cl_2 per molecule of complex was found during the X-ray analysis. The crystals are monoclinic with four [RuCl(NO)(CO)(**1**)] · CD_2Cl_2 units per cell in the $P2_1/n$ space group.

Table 6. *Crystal data for [RuCl(CO)(NO)(**1**)]* · CD_2Cl_2

Formula	$C_{46}H_{34}D_2Cl_3NO_2P_2Ru$	
Formula wt	906.18 amu	
Cell constants[a])	$a = 18.377(8)$ Å	$\beta = 113.50(5)°$
	$b = 12.698(4)$	$V = 4111.1(38)$ Å^3
	$c = 19.210(12)$	
Density	1.461 (calc.), 1.46(1) (exper.)[b]) gcm^{-3}	
Crystal dimensions	0.16 × 0.25 × 0.30 mm^3	
Radiation	Graphite monochromatized Mo*Ka* ($\lambda = 0.71069$ Å)	
μ (Mo*Ka*)	6.85 cm^{-1}	
θ_{max}	28°	
ω-scan range	0.9°	

[a]) Determined by a least-squares procedure from the measured angular positions of 15 reflections.

[b]) Measured by flotation in $CdCl_2$ solution.

3.4. *Intensity Measurements.* Lattice constants and intensities were measured with an automatic diffractometer Syntex $P2_1$ (details in *Table 6*). Three standard reflections remained constant throughout data collection. Data were processed as described previously [24], with $p = 0.0008$ as calculated from the variance of the standard reflections [25], and corrected for *Lorentz* and polarisation effects. Of the 10690 unique data collected, 5006 independent reflections with $I > 3\sigma(I)$ were used in the subsequeent analysis.

Table 7. *Positional parameters* ($\times 10^4$) *for non-hydrogen atoms* (standard deviations in parentheses)

	x	y	z		x	y	z
Non-group atoms							
Ru	802(0)	1731(1)	2733(0)	C(7)	-1256(5)	5369(7)	4435(5)
P(1)	-47(1)	265(1)	2689(1)	C(8)	-635(5)	5817(7)	4378(5)
P(2)	1387(1)	3371(2)	2607(1)	C(9)	357(5)	5930(7)	3826(5)
Cl	-116(1)	2021(2)	1388(1)	C(10)	681(5)	5602(7)	3344(5)
C	809(4)	2130(6)	3650(4)	C(11)	311(4)	4770(6)	2840(4)
O(1)	823(3)	2372(4)	4230(3)	C(12)	-336(4)	4257(6)	2881(4)
N	1729(4)	999(5)	2941(4)	C(13)	-1556(4)	2896(6)	3250(4)
O(2)	2323(4)	745(5)	3438(4)	C(14)	-2260(5)	2483(7)	3329(5)
C(1)	-1204(4)	2208(6)	2899(4)	C(15)	-639(4)	4506(6)	3432(4)
C(2)	-1499(4)	1238(6)	2607(4)	C(16)	-307(5)	5442(6)	3880(5)
C(3)	-2217(5)	907(7)	2654(5)	C(17)	-1258(4)	3929(6)	3556(4)
C(4)	-2567(5)	1518(7)	3012(5)	C(18)	-1590(5)	4414(7)	4044(5)
C(5)	-2577(5)	3051(7)	3788(5)	C(19)	-1120(4)	530(6)	2218(4)
C(6)	-2246(5)	3935(7)	4139(5)	C(20)	634(5)	4435(5)	2253(4)
Cl(1)	-2448(4)	3185(7)	1032(4)	chlorine atoms (occupancy 0.5) of the disordered solvent molecule			
Cl(2)	-1906(8)	4118(12)	452(7)				
Cl(3)	-1578(5)	4870(5)	825(4)				
Cl(4)	-726(9)	4504(10)	120(7)				

	x	y	z			x	y	z	
Rigid group atoms									
C(21)	108(3)	-344(4)	3598(2)	Ph(1)	C(33)	1826(3)	3264(4)	1903(2)	Ph(3)
C(22)	-516(2)	-767(8)	3745(3)		C(34)	2631(3)	3033(4)	2159(2)	
C(23)	-365(3)	-1270(7)	4433(3)		C(35)	2977(2)	2891(4)	1640(3)	
C(24)	410(3)	-1350(4)	4974(2)		C(36)	2518(3)	2980(4)	866(2)	
C(25)	1033(2)	-927(8)	4827(3)		C(37)	1713(3)	3211(4)	610(2)	
C(26)	882(3)	-425(7)	4139(3)		C(38)	1367(2)	3353(4)	1129(3)	
C(27)	34(3)	-863(4)	2108(3)	Ph(2)	C(39)	2185(3)	3949(4)	3430(3)	Ph(4)
C(28)	-215(4)	-1859(4)	2222(3)		C(40)	2513(3)	4897(4)	3331(2)	
C(29)	-178(4)	-2701(4)	1773(3)		C(41)	3117(3)	5369(4)	3943(3)	
C(30)	106(3)	-2545(4)	1209(3)		C(42)	3394(3)	4895(4)	4655(3)	
C(31)	355(4)	-1549(4)	1095(3)		C(43)	3066(3)	3948(4)	4755(2)	
C(32)	318(4)	-708(4)	1544(3)		C(44)	2462(3)	3475(4)	4142(3)	

	x	y	z	ϕ	θ	ψ
Rigid group parameters[a])						
Ph(1)	259(2)	-847(3)	4286(2)	180.8(3)	61.1(2)	5.4(3)
Ph(2)	70(2)	-1704(3)	1659(2)	180.1(2)	-33.8(2)	-67.9(2)
Ph(3)	2172(2)	3122(2)	1385(2)	78.0(2)	-0.6(2)	92.5(2)
Ph(4)	2789(2)	4422(3)	4043(2)	-36.6(2)	0.1(2)	122.2(2)

[a]) The coordinates x, y and z give the ring centers, and the angles ϕ, θ and ψ (in degrees) describe rotations about an internal coordinate system [30].

3.5. *Structure Analysis and Refinement.* The structure was solved by *Patterson* and *Fourier* methods and refined by least-squares. The isotropic refinement converged at R = 0.110. In the subsequent least-squares cycles only those atoms not belonging to the phenyl rings or to the benzo[*c*]phenanthrene system were refined anisotropically: convergence at R = 0.083. A difference map revealed four isolated peaks, which were interpreted as Cl atoms of CD_2Cl_2 in two disordered positions. In a second difference map the electron density did not exceed $\pm 3\sigma(\rho)$. At this stage (R = 0.073) H-atoms were positioned geometrically [26] and after two cycles repositioned: final R = 0.064 (Rw = 0.064). A three-block approximation of the normal equations matrix was used; the function minimized being $\sum w(|Fo| - |Fc|)^2$ with $w = 4Fo^2/\sigma^2(Fo^2)$. Phenyl rings were refined as rigid groups (D_{6h} symmetry, C–C = 1.392 Å). Atomic scattering factors and anomalous dispersion terms were taken from International Tables for X-ray Crystallography [27]. Calculations were performed, using local programs, on the UNIVAC 1110 computer of the University of Rome [28] and on the HP 21 MX minicomputer of the CNR Research Area [29]. Final positional parameters for non-hydrogen atoms are given in *Table 7.*

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