Discussion. The space group found in our structural determination is quite different from that previously established (triclinic, $P\bar{1}$, $a = 12·65$, $b = 12·25$, $c = 17·05$ Å, $\alpha = 76·25$, $\beta = 105·75$, $\gamma = 119·6°$, $Z = 2$, $R = 0·102$), and is not related to it by any simple transformation. It is not clear if this observation is related to the unusual circumstances in which our crystal was grown. The solvent from which the crystal was originally grown is not given.

The coordination at Pt is approximately trigonal, with P—Pt—P angles of 117·20 (6), 120·97 (6) and 121·83 (6)°, and the four atoms very close to co-planar. Pt—P distances ranged from 2·262 (2) to 2·271 (2) Å, similar to those previously noted in the other space group. The distances are somewhat shorter than those for bonds to PPh_3 in $[Pt(PPh_3)_2(Ph_2C{=}PAr)]$ [2·288 (3) and 2·294 (3) Å] (van der Knaap et al., 1984), presumably due to steric crowding in that species. Unlike the original structural determination there is no indication of any π–π interaction between pairs of benzene rings, and their orientations seem to be determined entirely with the object of minimizing steric interactions.

The structure may be compared with that of the related complex $[Pt(PCy_3)_3]$ (Immirzi et al., 1977), which was of considerably higher symmetry, with one of the independent molecules having C_3 crystallographic symmetry and the other two being close to C_3 symmetry. The bonds, as might be expected for this more hindered species, were slightly longer, 2·303 (3) Å. In both cases the molecules were close to perfectly planar and ligand repulsions were alleviated by meshing.

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Structure of [N,N'-Propylenebis(2-pyrrolylmethyleneaminato)]nickel(II)

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Abstract. [Ni(C$_{13}$H$_{14}$N$_4$)], $M_r = 284·98$, monoclinic, $P2_1/c$, $a = 10·096$ (2), $b = 9·360$ (2), $c = 30·565$ (4) Å, $\beta = 119·45$ (2)°, $V = 2515·1$ (9) Å^3, $Z = 8$, $D_x = 1·505$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu = 20·22$ cm^{-1}, $F(000) = 1168$, $T = 298$ (2) K, 437 parameters refined, final $R = 0·038$ for all 2587 reflections. The complex takes a square-planar geometry around the Ni atom. Although the coordination geometries of the two crystallographically independent complexes are quite similar to each other, significant differences in planarity and Ni—N distances are observed.

Introduction. Synthetic macrocyclic ligands containing pyrrole fragments are of interest as models

for the oxygenase, oxidase, and oxygen transport and storage proteins (Spiro, 1980; Sigel, 1981). A binucleating tetrapyrrolic macrocycle has recently been synthesized at this Institution (Acholla & Mertes, 1984), and the structure of the dicopper complex has been reported (Acholla, Takusagawa & Mertes, 1985). In order to compare the chemistry of the binuclear complex to its mononuclear analogue, [N,N'-propylenebis(2-pyrrolylmethyleneaminato)]-metal complexes were synthesized and the structure of the nickel(II) complex was determined.

Experimental. The title compound was synthesized by the method described by Weber (1967). A reddish brown crystal, ~0·1 × 0·1 × 0·05 mm, obtained by recrystallization from a 1:1 CH$_2$Cl$_2$–C$_6$H$_{12}$ mixed solution, was mounted on a glass fiber oriented approximately along [10$\bar{2}$]. Cell constants were

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Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2)

The thermal parameters are of the form $B = \frac{8}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B
Ni(A)	0·26049 (6)	0·04838 (6)	0·21825 (2)	4·32
N(1A)	0·1851 (3)	0·1373 (3)	0·2575 (1)	4·35
C(2A)	0·1198 (5)	0·2573 (5)	0·2605 (2)	5·52
C(3A)	0·0839 (5)	0·2479 (6)	0·2986 (2)	6·36
C(4A)	0·1312 (6)	0·1178 (6)	0·3204 (2)	6·60
C(5A)	0·1964 (5)	0·0501 (4)	0·2950 (1)	5·42
C(6A)	0·2604 (5)	-0·0818 (5)	0·2964 (2)	6·00
N(7A)	0·3004 (3)	-0·1079 (3)	0·2627 (1)	5·07
C(8A)	0·3690 (7)	-0·2459 (5)	0·2630 (2)	7·17
C(9A)	0·3382 (7)	-0·2892 (5)	0·2130 (2)	7·28
C(10A)	0·4018 (7)	-0·1945 (5)	0·1901 (2)	7·59
N(11A)	0·3384 (4)	-0·0491 (3)	0·1811 (1)	5·25
C(12A)	0·3342 (5)	0·0264 (5)	0·1449 (2)	5·57
C(13A)	0·2741 (4)	0·1632 (4)	0·1388 (1)	4·83
C(14A)	0·2608 (5)	0·2799 (5)	0·1090 (2)	6·16
C(15A)	0·1983 (5)	0·3884 (5)	0·1237 (2)	6·44
C(16A)	0·1807 (5)	0·3332 (5)	0·1618 (2)	6·01
N(17A)	0·2246 (3)	0·1983 (3)	0·1718 (1)	4·54
H(2A)	0·109 (4)	0·330 (4)	0·243 (1)	4·94
H(3A)	0·033 (4)	0·324 (4)	0·299 (1)	5·01
H(4A)	0·145 (6)	0·079 (5)	0·347 (2)	6·42
H(6A)	0·278 (3)	-0·149 (3)	0·323 (1)	4·09
H(8A)	0·355 (5)	-0·319 (6)	0·286 (2)	9·32
H(8A')	0·472 (5)	-0·234 (4)	0·279 (1)	5·72
H(9A)	0·230 (5)	-0·299 (4)	0·193 (1)	5·91
H(9A')	0·379 (5)	-0·393 (6)	0·218 (2)	9·29
H(10A)	0·407 (5)	-0·233 (5)	0·162 (2)	8·89
H(10A')	0·527 (7)	-0·186 (6)	0·212 (2)	11·32
H(12A)	0·381 (6)	-0·020 (5)	0·123 (2)	9·00
H(14A)	0·290 (4)	0·285 (3)	0·086 (1)	4·00
H(15A)	0·172 (4)	0·489 (5)	0·109 (1)	7·09
H(16A)	0·153 (4)	0·373 (4)	0·178 (1)	3·41
Ni(B)	0·37060 (6)	0·02816 (6)	0·02775 (2)	4·18
N(1B)	0·3682 (3)	-0·1620 (3)	0·0476 (1)	4·57
C(2B)	0·4600 (6)	-0·2646 (5)	0·0789 (2)	5·66
C(3B)	0·3847 (7)	-0·3962 (5)	0·0689 (2)	6·81
C(4B)	0·2397 (7)	-0·3720 (5)	0·0303 (2)	7·04
C(5B)	0·2311 (5)	-0·2274 (4)	0·0170 (2)	5·53
C(6B)	0·1263 (5)	-0·1381 (5)	-0·0207 (2)	6·06
N(7B)	0·1664 (3)	-0·0092 (4)	-0·0219 (1)	5·09
C(8B)	0·0589 (6)	-0·0881 (6)	-0·0612 (2)	6·88
C(9B)	0·1021 (7)	0·2414 (6)	-0·0489 (2)	7·88
C(10B)	0·2537 (5)	0·2787 (6)	-0·0434 (2)	6·63
N(11B)	0·3737 (4)	0·2114 (3)	0·0020 (1)	5·01
C(12B)	0·5052 (5)	0·2709 (5)	0·0261 (2)	5·27
C(13B)	0·6155 (4)	0·2043 (4)	0·0683 (1)	4·93
C(14B)	0·7645 (5)	0·2285 (6)	0·1053 (2)	6·63
C(15B)	0·8078 (5)	0·1208 (6)	0·1385 (2)	6·83
C(16B)	0·6821 (5)	0·0289 (5)	0·1210 (2)	5·66
N(17B)	0·5673 (3)	0·0783 (3)	0·0786 (1)	4·50
H(2B)	0·563 (5)	-0·246 (4)	0·101 (1)	6·43
H(3B)	0·426 (4)	-0·476 (4)	0·087 (1)	5·39
H(4B)	0·170 (5)	-0·441 (5)	0·012 (2)	7·22
H(6B)	0·039 (6)	-0·179 (5)	-0·039 (2)	8·31
H(8B)	0·071 (7)	0·088 (7)	-0·092 (2)	12·72
H(8B')	-0·035 (6)	0·053 (5)	-0·071 (2)	8·01
H(9B)	0·027 (6)	0·298 (6)	-0·072 (2)	9·56
H(9B')	0·128 (7)	0·273 (7)	-0·014 (3)	13·40
H(10B)	0·235 (6)	0·223 (6)	-0·071 (2)	9·44
H(10B')	0·277 (5)	0·385 (6)	-0·044 (2)	8·54
H(12B)	0·516 (3)	0·349 (4)	0·017 (1)	3·14
H(14B)	0·811 (4)	0·295 (4)	0·104 (1)	2·57
H(15B)	0·909 (6)	0·104 (5)	0·165 (2)	9·35
H(16B)	0·679 (4)	-0·055 (4)	0·132 (1)	4·17

determined by using 15 centered reflections widely scattered throughout reciprocal space $(35 > 2\theta > 25°)$. Preliminary counter data indicated a monoclinic system with systematic absences, $k = 2n + 1$ in $0k0$ and $l = 2n + 1$ in $h0l$, uniquely determining the space group as $P2_1/c$. Two octants $(h\ 0\rightarrow10,\ k\ 0\rightarrow8,\ l\ -26\rightarrow26)$ of data out to $2\theta = 100°$ were collected using a Syntex $P2_1$ diffractometer (Cu $K\alpha$, graphite monochromator) with θ–2θ scan mode [2θ scan angle: $(0·2823\tan\theta + 2·5)°$, scan speed: 1·0–

10·0° min^{-1}]. The background was estimated from the counts accumulated through the 1/6 of total scan at both edges of the peak. The total number of reflections measured was 3101. Lorentz and polarization factors were applied. Correction was made for a 2% decrease in intensity of two reflections monitored every 100 measurements. A semiempirical ψ-scan technique was used to correct for absorption (maximum and minimum correction factors: 1·224, 1·355) (North, Phillips & Mathews, 1968). 2587 independent F_o^2 data were obtained by merging equivalent reflections ($0kl$ zone). R_{int} for merging was 0·012, where $R_{int} = \Sigma(\Sigma_i^{n'} = 1 |\langle F_o^2\rangle - F_{oi}^2|)/\Sigma n'\langle F_o^2\rangle$. The reflections with $F_o^2 < 0·2\sigma(F_o^2)$ were reset to $F_o^2 = 0·2\sigma(F_o^2)$. The $\sigma(F_o^2)$ and $\sigma(F_o)$ values were defined as follows: $\sigma(F_o^2) = [\sigma_{count}^2 + (0·02F_o^2)^2]^{1/2}$ and $\sigma(F_o) = \sigma(F_o^2)/2F_o$. All reflections were used in subsequent calculations.

The positions of two crystallographically independent Ni atoms were determined by interpretation of a Patterson map. Successive difference Fourier syn-
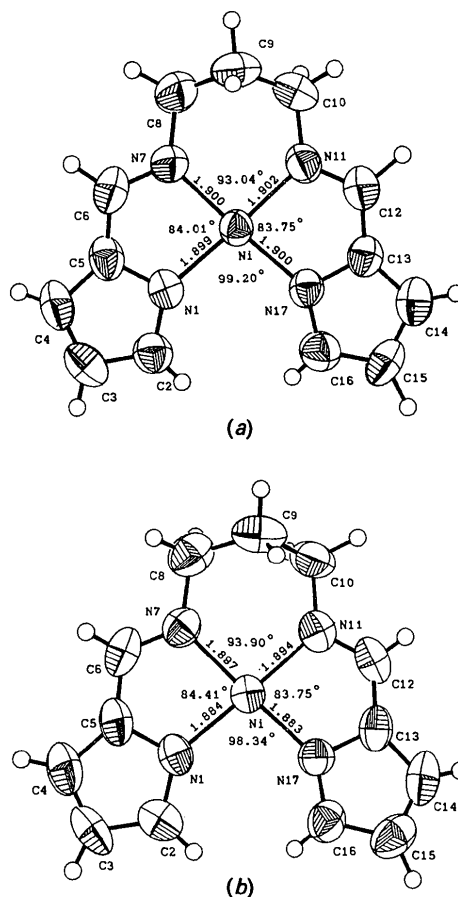

Fig. 1. Molecular configurations and adopted numbering schemes of the two crystallographically independent complexes of the title compound: (a) complex A, (b) complex B. The non-H atoms are shown with 74% probability thermal ellipsoids.

Table 2. *Distances (Å) from the least-squares plane defined by the four nitrogen atoms*

	Complex A	Complex B
Ni	−0·001 (3)	0·014 (3)
N(1)	−0·001 (3)	−0·077 (4)
C(2)	0·029 (5)	−0·267 (5)
C(3)	0·096 (5)	−0·418 (5)
C(4)	0·086 (5)	−0·289 (5)
C(5)	0·005 (4)	−0·095 (4)
C(6)	0·001 (5)	−0·023 (5)
N(7)	0·001 (4)	0·079 (4)
C(8)	−0·008 (6)	0·155 (5)
C(9)	0·648 (6)	0·674 (5)
C(10)	0·001 (6)	−0·173 (5)
N(11)	−0·001 (4)	−0·080 (4)
C(12)	−0·025 (4)	−0·213 (5)
C(13)	−0·038 (4)	−0·131 (4)
C(14)	−0·176 (5)	−0·168 (5)
C(15)	−0·193 (5)	0·033 (5)
C(16)	−0·098 (5)	0·190 (4)
N(17)	0·001 (4)	0·078 (4)

Fig. 2. Drawing of the crystal structure projected along the *b* axis. Two *A* complexes related to each other by a two-screw symmetry have an Ni(*A*)—Ni(*A*) distance of 6·311 Å. Two *B* complexes related to each other by a center of symmetry make a dimer with an Ni(*B*)—Ni(*B*) distance of 3·787 Å.

theses revealed the positions of all C and N atoms in the two independent molecules. All H atoms were located in difference maps computed after anisotropic refinement of non-H atoms, and were introduced into the refinement with isotropic thermal parameters. The parameters were refined by a full-matrix least-squares method. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma(F_o)^2$. Refinement was converged to $R = 0·038$, $wR = 0·051$, $S = 0·959$ for all data. The maximum Δ/σ in the last full-matrix least-squares refinement cycle is 0·07. The final difference Fourier map was featureless ($\pm 0·17$ e Å^{-3}). Atomic scattering factors including the anomalous-dispersion correction factor for the Ni atoms were taken from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a VAX 8650 computer at the academic computing center of the University of Kansas using programs of the *KUDNA* system (Takusagawa, 1984).

Discussion. The structure of [*N*,*N*'-propylenebis(2-pyrrolylmethyleneaminato)]nickel(II) has been determined. Final fractional coordinates with equivalent isotropic temperature factors are listed in Table 1. Bond distances and angles have been deposited.* The two crystallographically independent molecules are quite similar to each other as shown in Fig. 1. The complexes are coordinated in a square-planar fashion around Ni atoms. Deviations from the least-squares planes defined by the four N atoms are listed in Table 2. The crystal structure is shown in Fig. 2.

In complex *A*, the four N atoms are essentially planar, and Ni(*A*) sits in the plane. The four Ni—N

distances are identical within the e.s.d.'s. On the other hand, the four N atoms of complex *B* deviate significantly from the least-squares plane, and Ni(*B*) also deviates 0·014 (3) Å from the plane. Ni—N(pyrrole) distances [1·883 (4) and 1·884 (4) Å] are significantly shorter than Ni—N(imine) distances [1·897 (4) and 1·894 (5) Å] in complex *B*. This distortion from an idealized square-planar coordination might be related to the molecular packing as shown in Fig. 2. Two *B* complexes related to each other by a center of symmetry make a dimer with an Ni(*B*)—Ni(*B*) distance of 3·787 (2) Å. In the dimer, the Ni(*B*)'s deviate from the least-squares planes toward each other, decreasing the Ni—Ni distance. There is no such dimeric interaction in the *A* complexes.

It might be interesting to compare this structure with [*N*,*N*'-ethylenebis(2-pyrrolylmethylene-aminato)]nickel(II) which has an ethylene bridge instead of a propylene bridge in the ligand (Kabuto, Kikuchi, Yokoi & Iwazumi, 1984). This analogue also shows square-planar coordination. A significant difference in coordination geometry is observed for the N—Ni—N angles. The average angles of the title compound and the ethylene-bridged analogue are 98·8 *vs* 107·8° for N(pyrrole)—Ni—N(pyrrole) and 93·5 *vs* 84·7° for N(imine)—Ni—N(imine). The differences in N—Ni—N angles are quite rational since the propylene bridge is less strained than the ethylene bridge. The crystal structure of the ethylene-bridged analogue is a layered structure with spacing of about 3·5 Å. The Ni—N(imine) distances are considerably shorter in the ethylene-bridged compound (1·822 and 1·843 Å).

* Lists of anisotropic thermal parameters, complete molecular dimensions and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51932 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
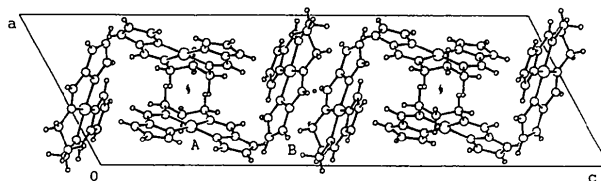
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Undecacarbonyl(triethylphosphine)- and -(trimethyl phosphite)-*triangulo*-triruthenium, [Ru₃(CO)₁₁PR₃] [R = Et (1), OMe (2)]: Substituent Effects on Ru—Ru and Ru—P Bond Lengths and Some Comments on the Effects of Refinement Models on Ru—C and C≡O Bond Lengths

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Abstract. (1), [Ru₃(CO)₁₁{P(C₂H₅)₃}], $M_r = 729.5$, triclinic, $P\bar{1}$, $a = 8.740\ (2)$, $b = 12.056\ (2)$, $c = 12.363\ (1)$ Å, $\alpha = 85.22\ (1)$, $\beta = 72.64\ (1)$, $\gamma = 72.73\ (1)°$, $V = 1187.3$ Å³, $D_x = 2.04$ g cm⁻³, $Z = 2$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 19.7$ cm⁻¹, $F(000) = 704$, $T = 298$ K, $R = 0.0219$ for 4950 observed $[I \geq 3\sigma(I)]$ reflections. (2), [Ru₃(CO)₁₁{P(OCH₃)₃}], $M_r = 735.4$, monoclinic, $P2_1/c$, $a = 16.621\ (2)$, $b = 7.992\ (2)$, $c = 18.124\ (3)$ Å, $\beta = 113.36\ (1)°$, $V = 2209.9$ Å³, $D_x = 2.21$ g cm⁻³, $Z = 4$, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 21.2$ cm⁻¹, $F(000) = 1408$, $T = 298$ K, $R = 0.0235$ for 4218 observed $[I \geq 3\sigma(I)]$ reflections. Both molecules contain slightly distorted triangular Ru₃ moieties with the phosphine and phosphite ligands equatorially substituted. Each Ru atom has distorted octahedral coordination geometry. The Ru1—Ru2, Ru1—Ru3, Ru2—Ru3 and Ru1—P bond lengths for (1) [values for (2) in square brackets] are: 2.9078 (2) [2.8883 (3)], 2.8648 (2) [2.8685 (3)], 2.8802 (2) [2.8735 (3)] and 2.3489 (5) Å [2.2750 (7) Å] respectively. The corresponding Ru2—Ru1—P bond angles are 112.80 (1)° [103.27 (2)°]. The observed Ru—P distances are consistent with a marked correlation between these distances and the Tolman cone angles for the P ligands in monosubstituted [Ru₃(CO)₁₁PR₃] complexes. Introduction of anisotropic displacement (thermal) parameters for the carbonyl ligands has resulted in small shifts of up to 0.02 Å in the positions of the C atoms towards the O atoms. The shifts are somewhat less than the effects commented upon by Braga & Koetzle [*Acta Cryst.* (1988), B44, 151–155].

Introduction. Electronic and steric effects shown by P-donor nucleophiles in their associative reactions with metal carbonyl clusters can be distinguished quantitatively by analysis of the dependence of the rate constants on pK_a and Tolman cone angle data (Tolman, 1977) for the nucleophiles (Brodie, Chen & Poë, 1988; Poë, 1988). Standard or intrinsic reactivities with respect to attack by a standard nucleophile can be obtained. The effects of substituents on the standard reactivities and on the electronic and steric effects can also be obtained so that the reactivity of any given cluster can be quantitatively characterized in this way. It will obviously be of interest to try and correlate reactivity effects of substituents with their structural effects and in the present paper the detailed X-ray analysis of two [Ru₃(CO)₁₁L] clusters [L = P(OMe)₃ and PEt₃] used in the kinetic studies are reported and discussed.

Experimental. The preparations of both compounds will be reported in detail elsewhere (Brodie, Chen & Poë, in preparation). Suitable crystals of (1) were obtained from a methanol/hexane solvent mixture (ca 1:1) over an extended period; those of (2) from a methanol/methylene dichloride solvent mixture.

Details of the unit-cell and space-group determinations and intensity data collections for both compounds are summarized in Table 1. Lorentz and polarization corrections were applied to all data measured; absorption corrections were not considered necessary in view of the regular shape of the crystals and the magnitude of μ for each compound. Both structures were solved by use of the Patterson function to locate the Ru atoms, and standard least-squares and Fourier methods to locate the remaining non-H atoms. H-atom positions obtained from ΔF maps were allowed to refine in the least squares.