51. Variable-Temperature and -Pressure ^{31}P-NMR Study of the Intramolecular PPh_3 Migration in the Cluster Compound $[Ir_2Rh_2(CO)_{11}PPh_3]$

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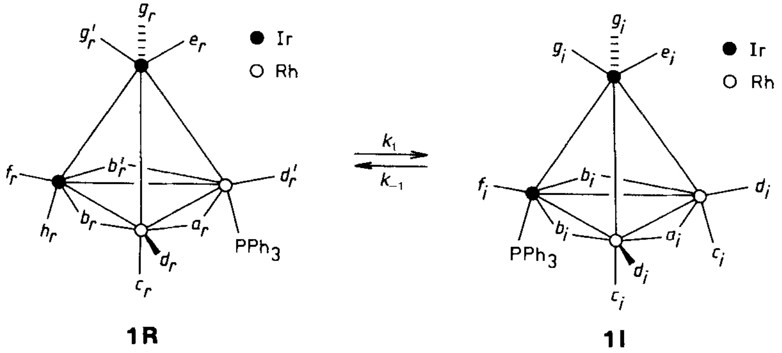
The reaction of $[Ir_2Rh_2(CO)_{12}]$ with 1 mol-equiv. of PPh_3 yields $[Ir_2Rh_2(CO)_{11}PPh_3]$ (**1**) as a mixture of two isomers with the phosphine ligand axially bound either to one basal Rh-atom in the kinetically preferred isomer **1R** or to one basal Ir-atom in the thermodynamically preferred isomer **1I**. Both isomers are fluxional on the ^{13}C-NMR time scale at low temperature due to CO scrambling. Around room temperature, a new type of fluxional process starts to operate which is responsible for the isomerisation **1R** $\rightleftarrows$ **1I**, *i.e.* the intramolecular migration of the reputedly inert PPh_3 ligand from one metal centre to another. The activation volumes of conversions **1R** → **1I** and **1I** → **1R** are both positive, indicating that the migration of PPh_3 is dissociative in character. This article reports the first application of variable pressure ^{31}P-NMR to mechanistic studies.

Introduction. – The fluxional behaviour of the cluster compounds derived from $[Ir_4(CO)_{12}]$ [1–3], $[Ir_3Rh(CO)_{12}]$ [4], $[Ir_2Rh_2(CO)_{12}]$ [5], and $[Rh_4(CO)_{12}]$ [6] are due to CO scrambling processes such as the merry-go-round of six CO's about a triangular face of the metal tetrahedron, changes of basal face, or the rotation of three terminal CO's located on one metal centre.

We report here on a new type of intramolecular rearrangement, distinct from CO scrambling, which was identified by a variable-temperature and variable-pressure ^{31}P-NMR study of the cluster compound $[Ir_2Rh_2(CO)_{11}PPh_3]$ (**1**).

Results and Discussion. – The reaction of $[Ir_2Rh_2(CO)_{12}]$ with 1 mol-equiv. of PPh_3 in CH_2Cl_2 at 0° followed by column chromatography at 0° gave $[Ir_2Rh_2(CO)_{11}PPh_3]$ as a single isomer **1R** (*Scheme*). The same isomer could also be obtained in slightly higher yield (75%) by reacting $[PPh_4][Ir_2Rh_2Br(CO)_{11}]$ [5] with PPh_3 and $AgBF_4$ (1 mol-equiv.) in CH_2Cl_2 at 0°. The same reactions effected at room temperature gave an equilibrium mixture of the two isomers **1I** and **1R** ($[\mathbf{1I}]/[\mathbf{1R}] \approx 3$) which could not be separated by chromatography or fractional crystallisation. The ^{31}P-NMR spectrum of a freshly prepared sample of **1R** in CD_2Cl_2 at 273 K consists of a *doublet* at δ +10.6 ppm ($^1J(P,Rh) = 119.3$ Hz) relative to external 85% H_3PO_4. The chemical-shift difference of the coordinated and free ligand ($\Delta\delta = +5.3$ ppm) suggests that the Rh-bonded PPh_3 ligand is located in axial position from a comparison with the corresponding $\Delta\delta$ values of $[Ir_4(CO)_{11}PPh_3]$ [6] and of the axial isomer of $[Ir_4(CO)_{11}PEt_3]$ [1a]. The ^{13}C-NMR spectrum of a sample of **1R** enriched in ^{13}CO (*ca.* 30%) in CD_2Cl_2 at 245 K presents 11 resonances of equal intensities (see *Exper. Part*). Three resonances with C,Rh-couplings have δ's in the region of bridging CO's indicating that two Rh-atoms and one Ir-atom form the basal face of the metal tetrahedron. Two of the three resonances with δ's in the region of radial CO's couple with Rh, and one of these two resonances presents an additional geminal coupling with ^{31}P. One resonance in the region of apical CO's is a *d* (^3J(C,P) = 37 Hz, *g'*) with a coupling constant typical of a CO group in pseudo-*trans*-position relative to a tertiary phosphine [1a]. Inspection of a COSY ^{13}C-NMR spectrum of **1R** where the only CO's which couple significantly are in relative pseudo-*trans*-positions (in particular, geminal ^2J(CO,CO) are very small [3]), reveals that two pairs of terminal CO's have relative pseudo-*trans*-position (*c*/*g* and *e*/*h* in the *Scheme*). All these observations confirm that the ground-state geometry of **1R** is of C_i symmetry with the PPh$_3$ ligand bonded to Rh in an axial position.

Scheme



Isomer **1R** is fluxional in solution since its ^{13}C-NMR spectrum at 273 K shows a broadening of all resonances (except that of carbonyl *a*). The fast CO scrambling process(es), which are probably similar to those observed in $[Ir_2Rh_2I(CO)_{11}]^-$ [5], could not be simulated as a new species starts to be present in significant amounts above 273 K. Indeed, if a sample of **1R** in CD_2Cl_2 is heated up to 311 K, a new *singlet* appears in the ^{31}P-NMR spectrum at δ −8.9 ppm, while the intensity of the *doublet* at +10.6 ppm decreases until equilibrium is reached (*Fig. 1*). This indicates that the kinetically favoured isomer **1R** converts to another isomer (**1I**, see *Scheme*) with the PPh$_3$ ligand now bonded to one Ir-atom. Seven additional resonances appear in the ^{13}C-NMR spectrum with relative intensities 1:2:2:1:2:2:1 (see *Exper. Part*). One *triplet* due to coupling to magnetically equivalent Rh-atoms and one *doublet* of *doublet*'s resulting from C,Rh and C,P couplings are observed in the region of bridging CO's with relative intensities 1:2. Two of the remaining signals with relative intensities 2:2 present couplings typical of terminal CO's bonded to Rh (^1J(C,Rh) = 64 and 75 Hz) and a third one shows pseudo-*trans* (^3J(C,P) = 31 Hz) coupling. These observations indicate that isomer **1I** has C_s symmetry with three edge-bridging CO's and the PPh$_3$ ligand bonded to the basal Ir-atom in axial position.

No other species, in particular no free PPh$_3$, were detected in the equilibrium mixture of **1R** and **1I**. Adding free PPh$_3$ to a solution of **1R** caused a rapid substitution of CO giving $[Ir_2Rh_2(CO)_{10}(PPh_3)_2]$ whose ^{13}C-NMR signals are clearly distinguishable from those of the monosubstituted complexes (see *Exper. Part*). The half-time of isomerisation **1R** ⇄ **1I** was found to be independent of the initial concentration of **1R** and did not vary

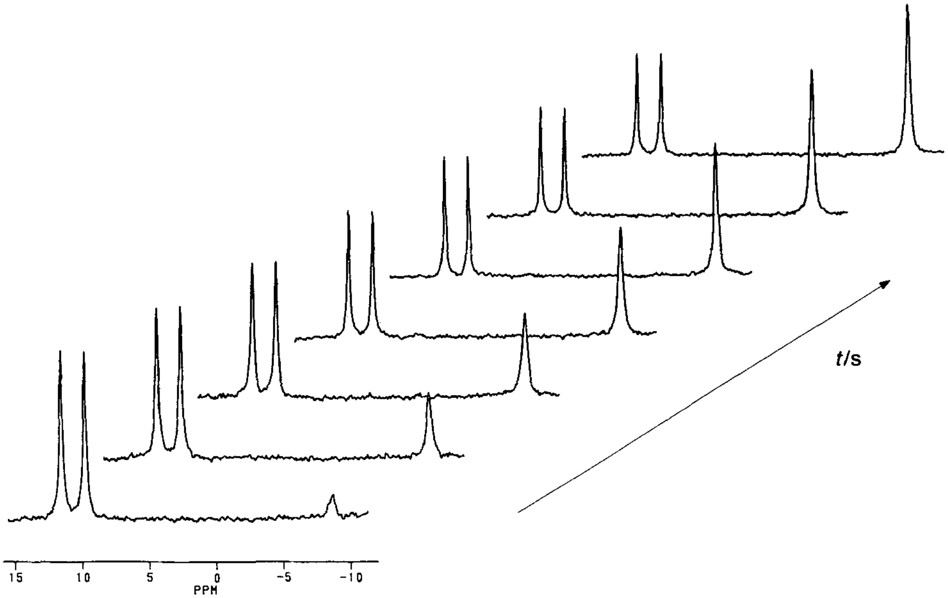


Fig. 1. *^{31}P-NMR Spectra of [$Ir_2Rh_2(CO)_{11}PPh_3$] at 330.4 K.* The time interval between two consecutive spectra is 4120 s.

in presence of H_2O_2 (5 mol-equiv.), which would selectively oxidize traces of free PPh_3 to $OPPh_3$. These observations indicate that the migration of PPh_3 between two metal centres, of which there is no other example to date, is an intramolecular process.

The mole fractions of **1R** were determined as a function of time at five temperatures (*Fig. 2*) by measuring the integrals of the ^{31}P signals of the two isomers. The rate constants of the forward (k_1) and reverse (k_{-1}) reactions of isomerisation were then calculated using *Eqn. 1* [7]

$$x_R = k_{-1}/(k_{-1} + k_1) + [1 - k_{-1}/(k_{-1} + k_1)] \exp[-(k_{-1} + k_1)(t + t_0)] \tag{1}$$

where x_R is the mol fraction of **1R** and t_0 the time lag between the sample preparation and the first spectrum (the temperatures used for sample preparation and for measurements were not always the same; therefore, t_0 had to be fitted as a parameter). The thermodynamic and kinetic parameters of isomerisation were calculated by fitting simultaneously all determined x_R values to *Eqns. 2–4*, using a nonlinear least-squares iterative procedure.

$$k^T_{1,-1} = (k_B T/h) \exp(-\Delta H^{\neq}_{1,-1}/RT + \Delta S^{\neq}_{1,-1}/R) \tag{2}$$

$$k^T_{1,-1} = k^{298}_{1,-1} \exp[(-\Delta H^{\neq}_{1,-1}/R)(1/T - 1/298.2)] \tag{3}$$

$$K^T = k^T_1/k^T_{-l}; \quad \Delta H^0 = \Delta H^{\neq}_1 - \Delta H^{\neq}_{-1}; \quad \Delta S^0 = \Delta S^{\neq}_1 - \Delta S^{\neq}_{-1} \tag{4}$$

where K^T is the ratio [**1I**]/[**1R**], ΔH^0 and ΔS^0 are the reaction enthalpy and entropy, respectively, $\Delta H^{\neq}_1$ and $\Delta S^{\neq}_1$ the activation parameters of reaction **1R** → **1I**, and $\Delta H^{\neq}_{-1}$ and $\Delta S^{\neq}_{-1}$ those of the reverse reaction.

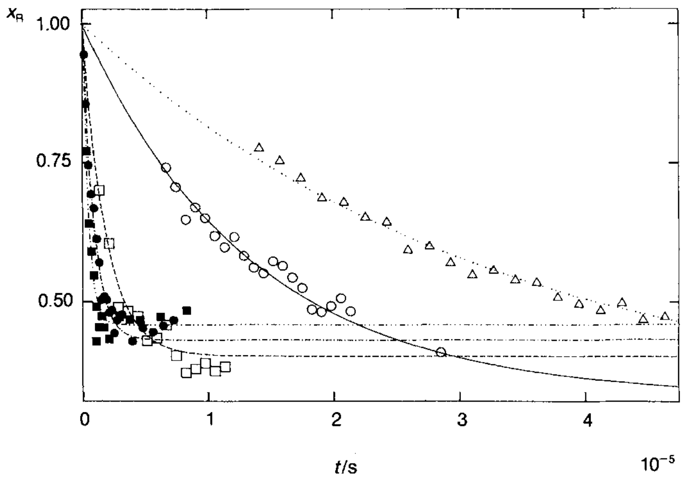


Fig. 2. *Mole fraction of isomer* **1R** *as function of time at five different temperatures* (△ = 305.0 K, ○ = 311.0 K, □ = 324.9 K, ● = 330.4 K, ■ = 335.7 K). The lines represent the calculated values using the parameters given in the *Table*.

The isomerisation was further studied as function of pressure (1–1840 bar). The rate constants k_1 and k_{-1} were determined at each pressure by fitting the x_R values to *Eqn. 5* [8]

$$\ln(k_{1,-1}) = \ln(k^0_{1,-1}) - \Delta V^{\neq}_{1,-1}\, P/RT \tag{5}$$

$$RT \ln(k_{1,-1}/k^0_{1,-1}) = -\Delta V^{\neq}_{1,-1}\, P \tag{6}$$

where $T = 324.0$ K, k^0_1 and k^0_{-1} are the rate constants at 1 bar, and $\Delta V^{\neq}_1$ and $\Delta V^{\neq}_{-1}$ the activation volumes for the forward and reverse reactions, respectively (*Fig. 3*). The activation volumes were deduced from the slope of the graph corresponding to *Eqn. 6*.

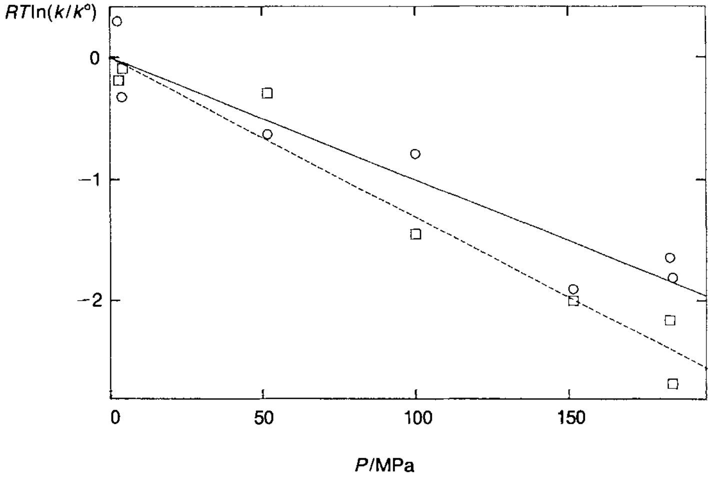


Fig. 3. *Pressure effect on the normalised logarithm of the formation rate constants for isomers* **1R** (□) *and* **1I** (○) *at 324.0 K.* The values found for $\ln(k^0_1)$ and $\ln(k^0_{-1})$ are +10.1 ± 1.5 and +13.2 ± 2.1, respectively.

Table. *Thermodynamic and Kinetic Parameters for the Isomerisation* **1R** ⇄ **1I** *in* CD_2Cl_2[a])

k_1 [s^{-1}]	$(7.7 \pm 0.3) \cdot 10^{-7}$	$\Delta V_1^{\#}$ [$cm^3 mol^{-1}$]	$+10.1 \pm 1.5$
k_{-1} [s^{-1}]	$(2.7 \pm 0.4) \cdot 10^{-7}$	$\Delta V_{-1}^{\#}$ [$cm^3 mol^{-1}$]	$+13.2 \pm 2.1$
$\Delta H_1^{\#}$ [kJ mol^{-1}]	$+109.6 \pm 1$	K_{298}	2.9 ± 0.6
$\Delta H_{-1}^{\#}$ [kJ mol^{-1}]	$+128.8 \pm 3$	ΔH^0 [kJ mol^{-1}]	-19.1 ± 2
$\Delta S_1^{\#}$ [J K^{-1} mol^{-1}]	$+ 6.2 \pm 4$	ΔS^0 [J K^{-1} mol^{-1}]	-55.4 ± 10
$\Delta S_{-1}^{\#}$ [J K^{-1} mol^{-1}]	$+ 61.5 \pm 11$	ΔV^0 [$cm^3 mol^{-1}$]	-3 ± 2

[a]) At 298 K, except for the ΔV's which were determined at 324 K.

The results are collected in the *Table*. The process **1R** → **1I** is exothermic, and the value of $(\Delta H^0 - T\Delta S^0)$ indicates that **1I** is the thermodynamically favoured isomer at 298 K. As expected, the reaction volume does not differ significantly from zero (this would not be the case if the ground-state of one isomer had all terminal ligands as observed for $[Ir_4(CO)_9\{\mu_3\text{-(1,3,5-trithiane)}\}]$ [9]). The smaller value of $\Delta H_1^{\neq}$ relative to $\Delta H_{-1}^{\neq}$ is in agreement with the more facile breaking of a Rh–P bond compared to an Ir–P bond. The positive values of $\Delta S_1^{\neq}$ and $\Delta S_{-1}^{\neq}$ suggests that the migration of the phosphine ligand from one metal centre to another is dissociative in character. The activation volumes are equal within experimental error and positive. Only a few activation volumes of organometallic reactions are available to date for comparison. A high-pressure NMR study of $[Ir_4(CO)_9\{\mu_3\text{-(1,3,5-trithiane)}\}]$ has shown that the minimal volume variation associated with the transformation of a bridging CO to an unbridged one in an intramolecular process is *ca.* 5 cm^3 mol^{-1} [9]. The activation volume of CO substitution by PPh_3 in $Cr(CO)_6$, where the Cr–CO bond is essentially broken in the transition state, is *ca.* 15 cm^3 mol^{-1} [10], and more recent values indicate a $\Delta V^{\neq}$ of *ca.* 20 cm^3 mol^{-1} for typical CO dissociative reactions [11]. We, therefore, propose that the exchange of PPh_3 in **1** takes place *via* breaking a M–PPh_3 bond in the rate-determining step, the phosphine ligand then migrating to an axial coordination site left vacant on an adjacent metal atom by the more rapid CO scrambling process.

In summary, these results show that a phosphine ligand, which is reputedly inert in a homometallic compound, may be mobile in a heterometallic cluster compound at room temperature. They also suggest that the μ_2-bonding mode of PPh_3 between heterometallic centres is energetically accessible, although there is no structural evidence to date for a μ_2-PPh_3 ligand in a cluster compound.

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Experimental Part

1. *General.* See [2]. $[Ir_2Rh_2(CO)_{12}]$ was prepared by the most recent literature method [5].

2. *Undecacarbonyl(triphenylphosphine)diiridiumdirhodium* ($[Ir_2Rh_2(CO)_{11}PPh_3]$, **1**). A soln. of $[Ir_2Rh_2(CO)_{12}]$ (291 mg, 0.26 mmol) and PPh_3 (68 mg, 0.26 mmol) in CH_2Cl_2 (55 ml) was stirred at 0° for 10 min. The red soln. was then evaporated at 0° and the solid residue chromatographed at 0° (column *Lobar, LiChroprep Si 60*, 40–63 µm, CH_2Cl_2/hexane 1:2). Recrystallisation from CH_2Cl_2/hexane at −25° gave **1**. Red microcrystals (210 mg, 69%). IR (CH_2Cl_2): 2087*m*, 2056*s*, 2022*s*, 1978 (sh), 1907*w*, 1866*m*, 1842*m* (CO). ^{31}P-NMR (CD_2Cl_2, 85% H_3PO_4 as external

reference): see text. ^{13}C-NMR (CD_2Cl_2, 245 K; for CO labels, see *Scheme*): 229.9 (*td*, *J*(C,Rh) = 29, *J*(C,P) = 9, a_r); 217.8 (*dd*, *J*(C,Rh) = 29, *J*(C,P) = 9, b'_r); 211.4 (*d*, *J*(C,Rh) = 28, b_r); 183.8 (*dd*, *J*(C,Rh) = 77, *J*(C,P) = 7, d'_r); 180.8 (*d*, *J*(C,Rh) = 75, d_r); 170.5 (*d*, *J*(C,Rh) = 71, c_r); 168.9, 167.9 (2*s*, f_r, g_r); 166.2 (*d*, *J*(C,P) = 37, g'_r); 161.7, 158.8 (2*s*, e_r, h_r). Anal. calc. for $C_{29}H_{15}Ir_2O_{11}PRh_2$ (1161.8): C 29.95, H 1.30, P 2.67; found: C 30.05, H 1.27, P 2.64.

The same reaction at 25° gave an equilibrium mixture of two isomers ([**1I**]/[**1R**] ≈ 3). Isomer **1I** was only identified in soln. ^{31}P-NMR: see text. ^{31}C-NMR (CD_2Cl_2, 245 K): 222.2 (*t*, *J*(C,Rh) = 29, a_i); 218.8 (*dd*, *J*(C,Rh) = 26, *J*(C,P) = 7, b_i); 180.8 (*d*, *J*(C,Rh) = 75, d_i); 170.5 (*d*, *J*(C,P) = 13, f_i); 168.5 (*d*, *J*(C,Rh) = 64, c_i); 167.9 (*s*, g_i); 159.9 (*d*, *J*(C,P) = 31, e_i); relative intensities 1:2:2:1:2:2:1.

Decacarbonylbis(triphenylphosphine)diiridiumdirhodium $[Ir_2Rh_2(CO)_{10}(PPh_3)_2]$. The formation of a red solid was observed upon adding PPh_3 (113 mg, 0.22 mmol) to a soln. of $[Ir_2Rh_2(CO)_{12}]$ (200 mg, 0.22 mmol) in hexane (100 ml) stirred at r.t. The solid was filtrated and dissolved in CH_2Cl_2 (3 ml). Prep. TLC (silica gel, CH_2Cl_2/hexane 1:1) gave $[Ir_2Rh_2(CO)_{10}(PPh_3)_2]$ (155 mg, 51 %), after recrystallisation from CH_2Cl_2/hexane at −25°. IR (CH_2Cl_2): 2067*m*, 2041*s*, 2010*s*, 1831*m* (CO). ^{31}P-NMR (CD_2Cl_2, 203 K): 8.3 (*d*, *J*(P,Rh) = 123.9); 19.0 (*t*, ^2J(P,Rh) = 10.2). ^{13}C-NMR (CD_2Cl_2, 200 K; sample enriched in ^{13}CO to *ca.* 30%): 230.8 (*t*, *J*(C,Rh) = 27); 226.6, 218.4 (2*d*, *J*(C,Rh) = 24 and 20.5, resp.); 184.9 (*dt*, *J*(C,Rh) = 78, ^3J(C,P) = 15); 181.8 (*dd*, *J*(C,Rh) = 75, ^2J(C,P) = 18); 173.8 (*d*, *J*(C,Rh) = 65); 169.6 (*d*, ^3J(C,P) = 37); 166.2, 160.2, 159.2 (3*s*); 160.0 (*d*, ^2J(C,P) = 5). COSY (CD_2Cl_2, 200 K, F_1 = 1488.1, F_2 = 2976.2 Hz): cross-peaks between the signals at 173.8 and 166.2 and between those at 160.0 and 159.2. These data indicate that this disubstituted complex has C_i symmetry with 3 edge-bridging CO's, 1 PPh_3 ligand bonded to a basal Rh-atom in axial position and the other one bonded to a basal Ir-atom in radial position.

3. *NMR Measurements.* The ^{31}P-NMR spectra at variable temp. were recorded using a *Bruker AC-200* spectrometer (4.7 T) working at 80.961 MHz. The measurements were made between 305.0 and 335.7 K. The variable-pressure NMR experiments were performed using a *Bruker AM-400* spectrometer (9.4 T) working at 161.923 MHz. The measurements were made up to 1840 bar using a home-built high-pressure probe designed for a *Bruker* wide-bore cryomagnet [8]. In this probe, the lower part contains the pressure bomb including the sample and the receiver coil positioned in the region of highest field homogeneity. The upper aluminium support fixed to the lower pressure seal by a four-pin plug contains the electronic frequency adapter box with the capacitive tuning

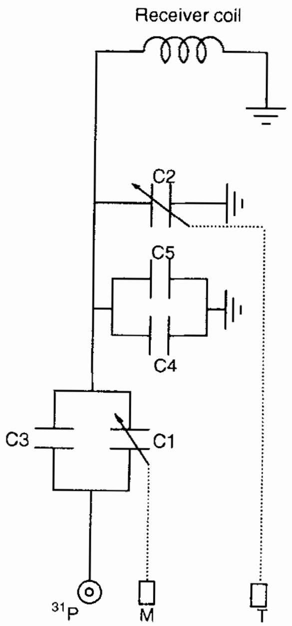

Fig. 4. *Electronic circuit for ^{31}P* (161.9 MHz) *detection in a high-pressure NMR probe, without field lock.* C1 and C2: 0.7–18 pF (*Polyflon*, New Rochelle, USA), C3 and C4: 5.6 pF; C5: 75 pF (*ATC*, Huntington Station, USA); M, T: matching/tuning screwdrivers for the adjustment from the top of the magnet.

network which is specific for a small frequency range. A new electronic circuit was developed for ^{31}P resonance (161.9 MHz) detection without field lock (*Fig. 4*). A built-in platinum resistor allowed temp. measurements with an accuracy of ± 1 K. By pumping a thermostated liquid through the bomb, the temp. was stabilized to ± 0.2 K at 324.0 K. The spectra were obtained by using 32 K data points resulting from 1000 to 2000 scans accumulated over a total spectral width of 5 kHz. To improve the signal to noise ratio, exponential filters (line-broadening) of 5 Hz were used. ^{31}P Chemical shifts are referred to 85% H_3PO_4 (external reference). The molalities of the solns. used for the variable-temp. and variable-pressure experiments were between 0.01 and 0.02 m.

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