indicate that the chelate rings in **1** are somewhat strained.

The Cu atom is displaced 0.2 Å from the equatorial plane defined by N(2), N(3), Cl(1), and Cl(2) in the direction of N(1). The Cu–Cl lengths are nonequivalent and are typical for equatorial Cu–Cl bonding.[13,14] This inequality may result from intermolecular hydrogen bonding (Table IV); Cl(2), with the longer Cu–Cl distance, participates in two relatively strong hydrogen bonds with amine H atoms, while Cl(1) participates in only one. The equatorial Cu–N bonds are approximately equal (2.063 (4), 2.038 (4) Å) and compare well with the values reported[4] for Cu([9]aneN$_3$)Br$_2$ (2.046 (4), 2.047 (4) Å) and for an ethylenediamine complex of Cu(II)[15] containing equatorial CuN$_2$Cl$_2$ units (2.054 (4), 2.081 (3) Å). The apical Cu–N(1) distance (2.268 (1) Å), while slightly longer than that in Cu([9]aneN$_3$)Br$_2$ (2.230 (4) Å) and substantially longer than the equatorial Cu–N bonds, may, as noted previously,[4] be anomalously shortened due to constraint by the macrocyclic triamine which causes the Cu–N(apical) bond to be tilted toward the basal N atoms.

In our view, the most significant feature of the structure is the elongated Cu–N(1) bond, a feature which is not common to all metal structures containing macrocyclic triamine ligands. Thus, bis[(*R*)-2-methyl-1,4,7-triazacyclononane]cobalt triiodide pentahydrate[16] and bis(isothiocyanato)(2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene)nickel(II)[17] contain nearly equal metal–N(macrocyclic) bonds within each complex, while μ-carbonato-bis(2,4,4,7-tetramethyl-1,5,9-triazacyclododec-1-ene)dicopper diperchlorate,[18] with a CuN$_3$O$_2$ unit structurally similar to that in **1**, exhibited substantially different equatorial (1.961 (7), 1.977 (7) Å) and apical (2.195 (7) Å) Cu–N distances.

A structural basis for the small formation constant of **1** is revealed by comparing the results reported here with those for (oxalato)(diethylenetriamine)copper(II)[19] tetrahydrate which contains approximately square-pyramidal CuN$_3$O$_2$ units with an apical O donor. Relative to **1**, the Cu–N distances are short (2.009 (8), 2.021 (7), 1.996 (8) Å) and the N–Cu–N angles are unstrained (85.2 (3), 85.0 (3)°). Thus, the flexible dien ligand achieves relatively strain-free meridional coordination with full equatorial Cu–N bonding.[20] In **1**, Cu–N bonding is attenuated by strain within the chelate rings and by the weak Cu–N interaction. These structural effects may be associated with thermodynamic and spectroscopic results reported for Cu(triamine)$^{2+}$(aq) complexes. Weaker Cu–N bonding in Cu([9]aneN$_3$)$^{2+}$(aq) relative to Cu(dien)$^{2+}$(aq) is consistent both with the respective $\Delta H°$ values of -13.0^{2} and -18.0^{21} kcal/mol and with the $\sim$1000-cm^{-1} red shift[2] in the Cu(II) d,d transition of Cu([9]aneN$_3$)$^{2+}$(aq) relative to Cu(dien)$^{2+}$(aq).

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Registry No. 1, 73002-72-9.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes and bond distances and angles involving H atoms (7 pages). Ordering information is given on any current masthead page.

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Electron Spin Resonance Studies of Some Ruthenium(III) Complexes

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The low-spin d^5 configuration is a good probe of molecular structure and bonding since the observed *g* values are very sensitive to small changes in the structure and to the metal–ligand covalency. Although a large number of d^5(t$_{2g}{}^5$) complexes have been studied, the application of electron spin resonance was mainly limited to the first-row transition series. Very few ruthenium(III) complexes have been subjected to ESR studies.[1-4]

In this paper we report an ESR study of a number of low-spin ruthenium(III) complexes containing triphenylarsine, triphenylphosphine, and β-diketonate (β-dk) ligands. Their geometries, ground states, and other spectral parameters have been obtained by using the ligand field theory for low-spin d^5 systems.

Experimental Section

The complexes studied in this work were prepared by the method already reported in the literature.[5-9] Tribromobis(triphenylarsine)ruthenium(III)–methanol [RuBr$_3$(AsPh$_3$)$_2$·CH$_3$OH] was prepared by the addition of methanol to a solution of RuBr$_3$(AsPh$_3$)$_3$ in dichloromethane and recrystallized from CH$_2$Cl$_2$–CH$_3$OH (yield 90%).

Reaction of RuX$_2$(β-dk)L$_2$ with Pyridine. An excess of pyridine (1–2 mL) was added to a solution of RuX$_2$(β-dk)L$_2$ (0.5 mmol) in 40 mL of CH$_2$Cl$_2$, and the resultant solution was heated to 70–80 °C for about 6–7 min. The solution was cooled, and an excess of methanol was added to get bright red crystals which were recrystallized from CH$_2$Cl$_2$–CH$_3$OH.

The complexes on analyses fit to a molecular formula RuX$_2$(β-dk)L(py) (yield 90%).

EPR Spectra. EPR spectra of the powdered samples and of the samples in CHCl$_3$ solution were recorded with a Varian Associates

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Table I. EPR Spectra of Some Ru(III) Complexes

complex		g_1	g_2	g_3	$\langle g \rangle^a$
$[RuCl_4(AsPh_3)_2]N(C_2H_5)_4$[b]	RT	2.49	2.49	1.73	2.26
	LN	2.50	2.50	1.71	2.27
$RuCl_3(AsPh_3)_2$[b]	RT	2.41	2.41	1.73	2.20
	LN	2.41	2.41	1.73	2.20
$RuCl_3(AsPh_3)_2(CH_3OH)$[b]	RT	2.46	2.46	1.67	2.23
	LN	2.52	2.25	1.71	2.28
fac-$RuCl_3(AsPh_3)_3$		2.53	2.53	1.73	2.29
mer-$RuCl_3(AsPh_3)_3$		2.74	2.38	1.75	2.33
$RuCl_3(AsPh_3)_2(OAsPh_3)$		2.57	2.23	1.65	2.18
mer-$RuBr_3(AsPh_3)_3$		2.60	2.35	1.73	2.26
$RuBr_3(AsPh_3)_2CH_3OH$		2.62	2.37	1.75	2.28
$RuBr_3(PPh_3)_2CH_3OH$		2.37	2.37	1.79	2.19
$RuCl_2(acac)(AsPh_3)_2$		2.31	2.31	1.89	2.18
$RuCl_2(dbm)(AsPh_3)_2$		2.27	2.27	1.87	2.14
$RuCl_2(ba)(AsPh_3)_2$		2.30	2.30	1.81	2.15
$RuCl_2(acac)(PPh_3)_2$		2.32	2.32	1.94	2.20
$RuCl_2(ba)(PPh_3)_2$		2.35	1.94	1.86	2.06
$RuBr_2(acac)(AsPh_3)_2$		2.37	2.37	1.93	2.23
$RuBr_2(ba)(AsPh_3)_2$		2.37	2.37	1.94	2.24
$RuBr_2(acac)(PPh_3)_2$		2.55	2.55	1.91	2.36
$RuBr_2(dbm)(PPh_3)_2$		2.41	2.41	1.93	2.26
$RuBr_2(ba)(PPh_3)_2$		2.39	2.39	1.92	2.24
$RuCl_2(dbm)(PPh_3)(py)$		2.45	2.31	1.79	2.20
$RuCl_2(dbm)(AsPh_3)(py)$		2.52	2.34	1.74	2.23

[a] $\langle g \rangle = [{}^1/_3 g_1{}^2 + {}^1/_3 g_2{}^2 + {}^1/_3 g_3{}^2]^{1/2}$. [b] Taken from ref 4. RT = 300 K; LN = 77 K.

Model V4502 EPR spectrometer at X-band frequencies. The spectra were calibrated by using a sample of DPPH ($g = 2.0036 \pm 0.0003$) which was taped to the sample holder. For all molecules of the type RuX_3L_3 and $RuX_3L_2(S)$ (where S = CH_3OH or $OAsPh_3$) the EPR measurements were taken on powdered samples since there was likelihood for these complexes to dissociate in solution.[3,4]

Results and Discussion

To interpret the EPR data, we use the theory as described by various authors[10-13] to determine the sign of g_i components and the correspondence between the experimental g values and g_x, g_y, and g_z components of the **g** tensor; we consider all possible combinations of experimental g values and their signs for acceptable results.

As a first approximation, the value of k was used for selecting one or more possible solutions. The results shown in Tables II and III are obtained by fixing the value of k in the range $0.5 < k < 2.0$.

In the ground state of the molecules, EPR absorption should correspond to transitions between the lowest Kramers doublet levels, as otherwise the parameters derived from the theory are physically unreal. Our calculations show that for a given combination of g values of the triphenylarsine complexes in Table II, the solution that corresponds to the lowest energy of the ground-state Kramers doublet (E) also yields the smallest value of k. For these molecules the axial distortion is about 3–4 times the spin–orbit coupling constant (λ), and the value of k is in the range 0.78–1.17.

For the β-diketonate complexes in Table III there are two acceptable fits. Fit 1 produces large Δ/λ ($\Delta > \lambda$) corresponding to a large axial distortion. The value of k is in the range 1.27–1.90, and the predicted energies of the electronic transitions are in the range 4000–8000 cm^{-1}. Fit 2 produces small Δ/λ ($\Delta < \lambda$) corresponding to small axial distortion. The value of k is in the range 1.1–1.2, and the estimated energy of the electronic transitions is around 1500 cm^{-1}. It is difficult to reject any of these on the basis of one single factor. However, one can make a choice on the basis of temperature-dependent magnetic susceptibility data. For molecules with $^2T_{2g}$ ground state a small distortion (fit 2) should show a large temperature-dependent second-order Zeeman contribution to the magnetic moments.[17] We have carried out magnetic studies[18] on some β-diketonate and bromotropolonate complexes of the type $RuX_2(dk)L_2$. The results show that these complexes are characterized by generally low and rather temperature-independent magnetic moments. This corresponds to a large distortion from O_h symmetry. Thus the magnetic data suggest the choice of fit 1 in Table III.

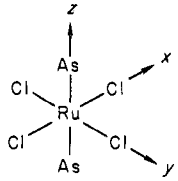

Figure 1. Stereochemistry of $RuCl_4(AsPh_3)_2^-$.

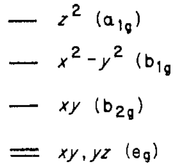

Figure 2. Energy level ordering of a tetragonally distorted octahedral complex.

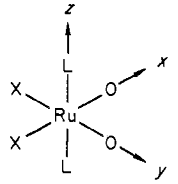

Figure 3. Stereochemistry of $RuX_2(\beta\text{-dk})L_2$ complexes.

One very good test for these calculations should be that the electronic transitions between the Kramers doublet should be observable.[1,15] But if the reduction of λ from the free-ion value is very small, which is quite likely because of the nature of the complexes under investigation, one would expect these transitions to fall in the IR or far-IR range of the spectrum. Such transitions are, therefore, likely to get obscured by vibrational transitions. In this context, we feel that the temperature-dependence study of magnetic susceptibility would be helpful in making a choice between rival solutions.

For most of the complexes studied the value of k is more than 1.0. This is quite surprising for complexes with such π-bonding ligands as PPh_3 and $AsPh_3$. Therefore, a direct correlation of orbital reduction factor and covalency was not possible from the available data. However, many other factors besides covalency are responsible for the variation in the value of k.[1,2,15,16]

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Table II. EPR Spectra of Ruthenium(III)–Triphenylarsine Complexes

compd[a]	g_x	g_y	g_z	k	Δ/λ	V/λ	E/λ	$\Delta E_1/\lambda$	$\Delta E_2/\lambda$	A	B	C
$RuCl_4(AsPh_3)_2^-$ RT	−2.49	2.49	−1.73	0.99	3.597	0.0	−3.75	3.41	4.25	0.212	0.977	0.0
LN	−2.50	2.50	−1.71	0.98	3.468	0.0	−3.63	3.29	4.13	0.221	0.975	0.0
$RuCl_3(AsPh_3)_2$	−2.41	2.41	−1.73	0.84	3.507	0.0	−3.66	3.32	4.16	0.218	0.976	0.0
$RuCl_3(AsPh_3)_2\cdot CH_3OH$ RT	−2.46	2.46	−1.67	0.87	3.190	0.0	−3.36	3.04	3.86	0.240	0.971	0.0
LN	−2.52	2.52	−1.71	1.02	3.489	0.0	−3.65	3.31	4.15	0.219	0.978	0.0
fac-$RuCl_3(AsPh_3)_3$	−2.53	2.53	−1.73	1.06	3.642	0.0	−3.79	3.45	4.29	0.210	0.978	0.0
mer-$RuCl_3(AsPh_3)_3$ a	−2.38	2.74	−1.75	1.17	4.114	2.148	−4.25	3.19	5.47	0.197	0.979	0.045
b	−2.74	2.38	−1.75	1.17	4.114	−2.148	−4.25	3.19	5.47	0.197	0.979	−0.045
$RuCl_3(AsPh_3)_2(OAsPh_3)$ a	−2.23	2.57	−1.65	0.78	3.262	1.728	−3.44	2.60	4.47	0.248	0.967	0.054
b	−2.57	2.23	−1.65	0.78	3.262	−1.728	−3.44	2.60	4.47	0.248	0.967	−0.054
mer-$RuBr_3(AsPh_3)_3$ a	−2.35	2.60	−1.73	0.97	3.722	1.463	−3.87	3.12	4.79	0.212	0.977	0.035
b	−2.60	2.35	−1.73	0.97	3.722	−1.463	−3.87	3.12	4.79	0.212	0.977	−0.035
$RuBr_3(AsPh_3)_2\cdot CH_3OH$ a	−2.37	2.62	−1.75	1.03	3.909	1.534	−4.05	3.26	4.99	0.202	0.979	−0.034
b	−2.62	2.37	−1.75	1.03	3.909	−1.534	−4.05	3.26	4.99	0.202	0.979	−0.034
$RuBr_3(PPh_3)_2\cdot CH_3OH$	−2.37	2.37	−1.79	0.83	3.964	0.0	−4.10	3.74	4.60	0.193	0.981	0.0

[a] See footnote *b* in Table I for explanation of RT and LN.

Table III. EPR Data for $RuX_2(\beta\text{-dk})L_2$ Complexes[a]

compd	fit	g_x	g_y	g_z	k	Δ/λ	E/λ	$\Delta E_1/\lambda$	$\Delta E_2/\lambda$	A	B
$RuCl_2(acac)As_2$	1	−2.31	2.31	−1.89	0.90	5.489	−5.59	5.19	6.09	0.137	0.990
	2	−2.31	2.31	1.89	1.13	0.147	−1.05	1.46	1.55	0.788	0.616
$RuCl_2(dbm)As_2$	1	−2.27	2.27	−1.87	0.74	4.924	−5.03	4.64	5.53	0.154	0.988
	2	−2.27	2.27	1.87	1.11	0.141	−1.05	1.46	1.55	0.789	0.614
$RuCl_2(ba)As_2$	1	−2.30	2.30	−1.81	0.71	4.076	−4.20	3.85	4.71	0.187	0.982
	2	−2.30	2.30	1.81	1.11	0.172	−1.06	1.45	1.56	0.783	0.622
$RuCl_2(acac)P_2$	1	−2.35	2.35	−1.94	1.38	7.914	−7.98	7.55	8.48	0.094	0.996
	2	−2.35	2.35	1.94	1.16	0.142	−1.05	1.46	1.55	0.789	0.614
$RuBr_2(acac)As_2$	1	−2.37	2.37	−1.93	1.36	7.321	−7.39	6.97	7.89	0.102	0.995
	2	−2.37	2.37	1.93	1.17	0.152	−1.05	1.45	1.56	0.787	0.617
$RuBr_2(ba)As_2$	1	−2.37	2.37	−1.94	1.48	8.018	−8.08	7.65	8.58	0.093	0.996
	2	−2.37	2.37	1.94	1.17	0.148	−1.05	1.45	1.56	0.788	0.616
$RuBr_2(acac)P_2$	1	−2.55	2.55	−1.91	1.90	6.965	−7.04	6.62	7.54	0.107	0.994
	2	−2.55	2.55	1.91	1.26	0.213	−1.08	1.44	1.58	0.774	0.633
$RuBr_2(dbm)P_2$	1	−2.41	2.41	−1.93	1.53	7.500	−7.57	7.142	7.57	0.099	0.995
	2	−2.41	2.41	1.93	1.19	0.170	−1.05	1.45	1.56	0.780	0.615
$RuBr_2(ba)P_2$	1	−2.39	2.39	−1.92	1.27	6.399	−6.48	6.07	6.98	0.117	0.993
	2	−2.39	2.39	1.92	1.18	0.165	−1.06	1.45	1.56	0.784	0.620

[a] For all the complexes $V/\lambda = 0$ and $C = 0$. E is the energy of the ground Kramers doublet. As = $AsPh_3$; P = PPh_3.

For all axially symmetric molecules, our results show that the hole is in the $t_2^0(d_{xy})$ orbital and the sign of g_y is positive and both g_x and g_z are negative ($B > A, C$). The large negative value of Δ indicates a ^2B (or an ^2A) ground term. The ordering of the one-electron real functions is the one where the doubly degenerate level $t_2^{\pm}(d_{xz} \pm d_{yz})$ lies the lowest. The orbital energies of some of the molecules are given in Table IV.

Due to highly directional nature of the metal-to-phosphine bond and also due to the lower energy of the empty d orbital of phosphorus, which are potentially more effective in π bonding than those of halogens, triphenylphosphines and triphenylarsines have a much greater ligand field strength than those of β-diketonates and halogens.[25,26] If the axes of the molecule are as defined in Figure 1, one would expect energy level ordering as in Figure 2 as a consequence of different ligand fields in the three planes.[1] The ground-state electronic configuration is then $(e_g)^4(b_{2g})^1$, leading to a $^2B_{2g}$ ground term. By using simple expression[4] for $g_\perp$, one can show that the axial splitting (Δ) is about 4 times the spin–orbit coupling constant (λ). Thus the proposed energy level scheme for the molecule is in agreement with the calculated results (Tables II and IV).

Similarly, for the β-diketonate complexes if one assumes a stereochemistry as in Figure 3, one gets the following: the *xy* plane contains two halogen atoms and two oxygen atoms; *xz* and *yz* planes contain two phopshine (or arsine) groups, one halogen atom, and one oxygen from the β-diketone. The energy level scheme proposed on the basis of this stereochemistry is in agreement with the results in Table III.

Table IV. Calculated d-Orbital Energies

compd		symmetry	E (λ), cm^{-1}	d-orbital order
$RuCl_4(AsPh_3)_2^-$		D_{4h}	−1.20, 2.40	e(*xz*,*yz*) < b_2(*xy*)
$RuCl_3(AsPh_3)_2$		C_{2v}	−1.17, 2.34	e(*xz*,*yz*) < b_2(*xy*)
fac-$RuCl_3(AsPh_3)_3$		C_{3v}	−1.21, 2.42	$t^{\pm} < t_0(d_{z^2})$
mer-$RuCl_3(AsPh_3)_3$	a	C_{2v}	−2.44, 0.30, 2.74	*yz* < *xz* < *xy*
	b	C_{2v}	−2.44, 0.30, 2.74	*xz* < *yz* < *xy*
mer-$RuBr_3(AsPh_3)_3$		C_{2v}	−1.97, 0.51, 2.48	*xz* < *yz* < *xy*
$RuCl_2(acac)(AsPh_3)_2$			−1.83, 3.66	*xz*, *yz* < *xy*
$RuCl_2(ba)(AsPh_3)_2$			−1.36, 2.72	*xz*, *yz* < *xy*
$RuCl_2(dbm)(AsPh_3)_2$			−1.64, 3.28	*xz*, *yz* < *xy*
$RuCl_2(acac)(PPh_3)_2$			−2.64, 5.28	*xz*, *yz* < *xy*
$RuBr_2(acac)(PPh_3)_2$			−2.32, 4.64	*xz*, *yz* < *xy*

If the two phosphines (or arsines) are trans to each other, then they should compete for the same d orbitals of the central metal ion. Because of this trans influence,[27] it should be possible to replace one of the phosphines (or arsines) by a ligand with different π-bonding ability. When the β-diketonate complexes are reacted with pyridine in dichloromethane so-

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lution at around 70–80 °C, the following reaction takes place:

$$\mathrm{RuX_2(\beta\text{-}dk)L_2 + py \xrightarrow{80\ ^\circ C} RuX_2(\beta\text{-}dk)L(py) + L}$$

This reaction is quite interesting because this suggests the stereochemistry as proposed in Figure 3 and shows the presence of loosely bound phosphine or arsine in these molecules. It is interesting to note that molecules of the type MX_3L_3 also have loosely bound PPh_3 or $AsPh_3$ ligands and dissociate in solution:

$$MX_3L_3 \rightarrow MX_3L_2 + L$$

The reason for this lability is trans influence and/or steric effect of the bulky PPh_3 (or $AsPh_3$) groups. The role of such loosely bound ligands in a complex will be to distort the molecules from the idealized geometry—a fact confirmed by the EPR results in Tables II and III. Such molecules are likely to be highly reactive because they are in the so-called[29] entatic state (a term which refers to similar situation for metal ions in an enzyme).

For molecules with three distinct components we found two solutions a and b, where the results are not very much different from each other. The highest lying orbital is d_{xy}, and the ground state may be either (a) d_{yz} or (b) d_{xz}. It is not possible to decide between the two possibilities. However, it was possible to distinguish between the facial and meridional isomers of $RuCl_3(AsPh_3)_3$. The facial isomers have C_{3v} symmetry. On the basis of the trigonal model,[28] the hole is in the $t_2{}^0(d_{z^2})$ orbital, leaving d_{xz}, d_{yz} lowest. The electronic configuration is $(e)^4(a_1)^1$ which implies a ^2A ground term. The meridional isomers show rhombic distortion ($g_x \neq g_y \neq g_z$). There is a significant difference between the relative d-orbital energies of the facial and meridional isomers (Table IV). The large difference in the value of k in these two isomers cannot be given any simple interpretation.

Conclusion

In this paper we have presented experimental results of a large number of Ru(III) complexes containing triphenylphosphine or triphenylarsine as one of the ligands. The results show a large axial distortion and a ^2B (or an ^2A) ground term for these complexes. The low-symmetry ligand field component is larger than the spin–orbit coupling constant ($\Delta > \lambda$). There may be two contributing factors for the large axial distortion: (1) a geometric factor and (2) anisotropy in the covalent bonding.[2] The anisotropy in covalent bonding probably plays an important role in distorting the molecules. Unfortunately it was not possible to estimate covalency because of the possible influence of CI and CT states.

The present ligand field model for interpreting the magnetic data was not quite successful in estimating the orbital reduction factor. From the EPR and magnetic susceptibility data it was felt that inclusion of configurational and charge-transfer mixing into the theory is worthy of further attention.

Registry No. *fac*-$RuCl_3(AsPh_3)_3$, 72747-39-8; *mer*-$RuCl_3(AsPh_3)_3$, 61769-11-7; $RuCl_3(AsPh_3)_2(OAsPh_3)$, 61730-99-2; *mer*-$RuBr_3(AsPh_3)_3$, 72747-40-1; $RuBr_3(AsPh_3)_2CH_3OH$, 15692-69-0; $RuBr_3(PPh_3)_2CH_3OH$, 15692-71-4; $RuCl_2(acac)(AsPh_3)_2$, 72747-41-2; $RuCl_2(dbm)(AsPh_3)_2$, 72747-42-3; $RuCl_2(ba)(AsPh_3)_2$, 72747-43-4; $RuCl_2(acac)(PPh_3)_2$, 72747-33-2; $RuCl_2(ba)(PPh_3)_2$, 72748-18-6; $RuBr_2(acac)(AsPh_3)_2$, 72747-34-3; $RuBr_2(ba)(AsPh_3)_2$, 72747-35-4; $RuBr_2(acac)(PPh_3)_2$, 72747-36-5; $RuBr_2(dbm)(PPh_3)_2$, 72747-37-6; $RuBr_2(ba)(PPh_3)_2$, 72747-38-7; $RuCl_2(dbm)(PPh_3)(py)$, 72692-65-0; $RuCl_2(dbm)(AsPh_3)(py)$, 72708-36-2; $RuBr_3(AsPh_3)_3$, 63632-06-4.

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Phosphane Adducts with Vanadium, Niobium, and Tantalum Tetrachlorides: Synthesis and Study by Electron Spin Resonance

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A large number of transition-metal halides are known to give molecular adducts of well-defined stoichiometry with a variety of phosphorus-donor ligands such as phosphanes or phosphites. These compounds are of great interest as precursors in the synthesis of highly reactive low-valent metal complexes whose role in homogeneous catalysis and activation of chemically inert molecules is not to be emphasized. Surprisingly, phosphane adducts of the vanadium group did not appear to receive hitherto much attention.[1-3] It is noteworthy that ESR methods are particularly well adapted for their study because of their simple electronic configuration (d^1) and the high isotopic ratio of the metal having a nuclear magnetic moment.

Earlier we reported[4] that $NbCl_4$ coordinates with two molecules of PR_3 (R = *n*-butyl, isobutyl) to form $NbCl_4{\cdot}2PR_3$ adducts of octahedral geometry, well characterized from their room- and low-temperature ESR spectra. We report here[5] on the formation of adducts of the general formula $MCl_4{\cdot}2Pr_3$ (M = V, Nb, Ta; R = ethyl) and show that significant information can be obtained from ESR and UV–visible spectra about their molecular geometry and ligand–metal interaction, allowing comparison to be made in a homogeneous series of compounds going down the periodic table. Furthermore, our results report on what to our knowledge is the first example of metal–ligand interaction detectable by ESR in a third-row transition-metal compound.

Experimental Section

All manipulations were performed under argon. Commercial VCl_4 (Alfa Inorganics) was used without further purification. $NbCl_4$ and $TaCl_4$ were prepared by the reduction of the respective pentahalides with aluminum foil according to literature methods. ESR spectra were recorded on a JEOL ME 3X X-band spectrometer with Bruker B-A6 accessory for field calibration. UV-visible spectra were recorded on a Cary 14 spectrometer in toluene solutions.

Results and Discussion

Vanadium and niobium tetrachlorides react with stoichiometric amounts (1:2) of triethylphosphine in toluene, and tantalum tetrachloride reacts with excess phosphine (as solvent, the reaction does not appear to take place in toluene) to yield colored solutions whose study by ESR reveals the nature of the species formed. The solution spectra at room temperature (Figure 1) are well resolved and exhibit hyperfine splitting due to interaction of the unpaired electron with the metal nuclei (^{51}V, ^{93}Nb, and ^{181}Ta) as well as superhyperfine splitting (for V and Nb only) due to interaction with two ^{31}P nuclei of the phosphane ligands. At −130 °C the frozen solution spectra display features due to parallel and perpendicular components indicative of axially symmetric molecular geometry and patterns which suggest the formation of 1:2 adducts in all three compounds. Phosphorus superhyperfine splitting is neatly resolved on both the high- and the low-field parallel components of the vanadium compound and only on the low-field part in the niobium and tantalum compounds. The ESR

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