keeping with the reactivities observed for other N-bonded complexes of this kind, $[(NH_3)_5CoNH_2SO_2NH_2]^{3+}$, $[(NH_3)_5CoNH_2SOCH_3]^{3+}$, $[(NH_3)_5CoNH_2CONR_2]^{3+}$, and $[(NH_3)_5CoNH_2CO(OC_2H_5)]^{3+}$, all of which have a very acidic proton ($pK'_a \leq 3$) on the nitrogen bound to Co.[6] The amidine complexes, on the other hand, are very much less reactive ($t_{1/2} > 10$ h) and less acidic. The apparent correlation between reactivity and acidity breaks down with complexes such as amide-*N* species, which, although quite acidic, are not very reactive.[6] However, we have argued that the protonated amidine and amide complexes are each of the Co—NH= kind, and all these results can be rationalized if the Co—NH_2R bond (electron-withdrawing R) is appreciably weaker than the Co—NH= bond and the reactions have an appreciable dissociative component.

Experimental Section

Electronic spectra were measured by Cary 210 and Cary 118C instruments, thermostated to 25.0 ± 0.1 °C by water circulation from Lauda baths. Details of our kinetic techniques and data analysis are described elsewhere.[2,6] The hydrolysis reactions were sufficiently slow to follow in situ in a cell thermostated within the spectrophotometer and were monitored at 520 nm by using 0.1–0.32 M $HClO_4$ at constant ionic strength (1.17 M; $NaClO_4$). Reported specific rates are the means of quadruplicate determinations. The chromatography (below) and final spectra were consistent with 100% $[(NH_3)_5CoOH_2]^{3+}$ as product (ϵ_{490} 47.7). NMR spectra were recorded on either Varian T60 (^1H; probe temperature 30 °C) or Varian XL-300 (^{13}C, ^1H; probe temperature 20 °C) instruments for Me_2SO-d_6 solutions using dioxane (^{13}C) or tetramethylsilane (^1H) as the internal references. Chemical shifts are reported as positive downfield from TMS (^1H) or dioxane (^{13}C). Chemicals were AnalaR grade or the equivalent. Cation-exchange chromatography was carried out with use of SP Sephadex C25 (Na^+ form) cation resin and 0.23 M Na^+ eluant (pH 7; 0.01 M $H_2PO_4^-$, 0.01 M HPO_4^{2-}, 0.2 M Cl^-). Salts of the nitrile complex ions $[(NH_3)_5CoNCR]^{3+}$ were obtained from $[(NH_3)_5CoOSO_2CF_3](CF_3SO_3)_2$[21] as perchlorate or trifluoromethanesulfonate salts as described elsewhere.[7]

$[(NH_3)_5CoNH{=}C(NH_2)R](ClO_4)_3$. $[(NH_3)_5CoNCR](ClO_4)_3$ (2.0 g) was dissolved in NH_3(l) (ca. 50 mL) in an open but narrow-necked flask. Within minutes the solution changed color from yellow to orange-yellow. The ammonia was allowed to evaporate and the treatment with NH_3(l) repeated. The residue was recrystallized from a minimum volume of water with use of either aqueous $NaClO_4$ or $HClO_4$ as precipitant. Samples contaminated with a small amount of $[(NH_3)_5CoOH_2](ClO_4)_3$ were recrystallized from water/$NaClO_4$ containing Tris (0.02 M), which kept the aqua complex in solution as its more soluble hydroxo form. Some of the products proved to be hydrates, as shown by ^1H NMR spectroscopy in dry Me_2SO, but lattice water was removed under vacuum over P_2O_5. Anal. Calcd for $[(NH_3)_5CoNH{=}C(NH_2)CH_3](ClO_4)_3$: C, 4.80; H, 4.20; N, 19.58; Cl, 21.28. Found: C, 4.60; H, 4.36; N, 19.30; Cl, 21.13. Visible spectrum: ϵ_{484}(max) 77.5 (0.01 M $HClO_4$).

$[(NH_3)_5CoNH{=}C(NH)R](ClO_4)_2$. Only the methyl and *o*-nitrophenyl derivatives were characterized. To a thin slurry of the protonated form in water was added 1 M NaOH dropwise until it just dissolved. (N.B. Too much OH^- can lead to decomposition.) The solution, which had darkened, was filtered and treated with a $^1/_5$ volume of saturated aqueous $NaClO_4$. Crystals deposited readily, and after they were cooled at 0 °C for 30 min, these were collected, washed with ethanol and ether, and dried over P_2O_5 under vacuum. Visible spectrum: ϵ_{485}(max) 83.0 (R = CH_3, 0.1 M NaOH).

$[(NH_3)_5CoN{=}C(NH_2)N(CH_3)_2](ClO_4)_2{\cdot}H_2O$ and $[(NH_3)_5CoN{=}C(NH_2)N(CH_3)_2](CF_3SO_3)_2{\cdot}H_2O$. This material was prepared exactly as described for the amidines except one treatment with NH_3(l) was sufficient, and the product was recrystallized from a minimum volume of aqueous Tris (0.02 M) with either aqueous $NaCF_3SO_3$ or $NaClO_4$ as the precipitant to afford deep burgundy crystals, which were air dried (each was a monohydrate; ^1H NMR spectroscopy in dry Me_2SO). Visible spectrum: ϵ_{511}(max) 102.0 (0.1 M Tris).

Attempts to prepare the methyl amidine and dimethylguanidine complexes directly from the free ligands with use of standard synthetic practices yielded only $[(NH_3)_5CoOH](ClO_4)_2$.

Acknowledgment. This work was supported by the Australian Research Grants Scheme.

Registry No. $[(NH_3)_5CoNCN(CH_3)_2](ClO_4)_3$, 123881-63-0; $[(NH_3)_5CoNCCH_3](ClO_4)_3$, 15663-50-0; $[(NH_3)_5CoNCCH{=}CH_2](ClO_4)_3$, 15648-92-7; $[(NH_3)_5CoNCC_6H_5](ClO_4)_3$, 38363-82-5; $[(NH_3)_5CoNCC_6H_4$-*o*-$NO_2](ClO_4)_3$, 84935-04-6; $[(NH_3)_5CoNCC_6H_4$-*p*-$F](ClO_4)_3$, 123881-65-2; $[(NH_3)_5CoNH{=}C(NH_2)N(CH_3)_2](ClO_4)_3$, 123881-67-4; $[(NH_3)_5CoNH{=}C(NH_2)CH_3](ClO_4)_3$, 123881-69-6; $[(NH_3)_5CoNH{=}C(NH_2)CH{=}CH_2](ClO_4)_3$, 123881-71-0; $[(NH_3)_5CoNH{=}C(NH_2)C_6H_5](ClO_4)_3$, 123881-73-2; $[(NH_3)_5CoNH{=}C(NH_2)C_6H_4$-*o*-$NO_2](ClO_4)_3$, 123881-75-4; $[(NH_3)_5CoNH{=}C(NH_2)C_6H_4$-*p*-$F](ClO_4)_3$, 123881-77-6; $[(NH_3)_5CoNH{=}C(NH)CH_3](ClO_4)_2$, 123881-79-8; $[(NH_3)_5CoNH{=}C(NH)C_6H_4$-*o*-$NO_2](ClO_4)_2$, 123881-81-2; $[(NH_3)_5CoN{=}C(NH_2)N(CH_3)_2](ClO_4)_2$, 123881-83-4; $[(NH_3)_5CoN{=}C(NH_2)N(CH_3)_2](CF_3SO_3)_2$, 123881-84-5; NH_3, 7664-41-7; $NCN(CH_2)$, 1467-79-4; $NCCH_3$, 75-05-8; $NCCH{=}CH_2$, 107-13-1; NCC_6H_5, 100-47-0; NCC_6H_4-*o*-NO_2, 612-24-8; NCC_6H_4-*p*-F, 1194-02-1; $NH{=}C(NH_2)CH_3$, 143-37-3; $NH{=}C(NH_2)C_6H_4$-*o*-NO_2, 88718-94-9; $NH{=}C(NH_2)N(CH_3)_2$, 6145-42-2.

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Contribution from the Departments of Chemistry,
University of Modena, Modena, Italy,
and University of Florence, Florence, Italy

Synthesis, Crystal and Molecular Structure, and Magnetic Properties of Bis[tris(μ-3,5-diamino-1,2,4-triazole-N^1,N^2)tris(thiocyanato-*N*)nickel(II)]nickel(II) Hexahydrate

L. Antolini,[1a] A. C. Fabretti,*,[1a] D. Gatteschi,*,[1b] A. Giusti,[1a] and R. Sessoli[1b]

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1,2,4-Triazoles have been actively investigated as versatile ligands that can yield polynuclear metal complexes with interesting magnetic properties.[2-7] In particular, it was found that three 1,2,4-triazoles can bridge between two metal ions, yielding dimeric and trinuclear species.[6,7] In order to prevent such a coordination and to favor the formation of thiocyanate bridges, Reedijk et al.[8] successfully used the strategy to employ bulky 3,5-disubstituted 1,2,4-triazoles. In particular, they isolated a compound of formula $Ni_3(detrH)_6(NCS)_6{\cdot}2H_2O$ (detrH = 3,5-diethyl-1,2,4-triazole), in which the central and terminal ions are bridged by two triazoles and one thiocyanate ion, while the terminal nickel ions complete their octahedral coordination with one triazole and two thiocyanate atoms. We have now found that using 3,5-diamino-1,2,4-triazole, guanazole, as a ligand yields a compound of formula $Ni_3(guanazole)_6(NCS)_6{\cdot}6H_2O$, which, notwithstanding the close similarity in the formula to $Ni_3(detrH)_6(NCS)_6{\cdot}2H_2O$, has three bridging guanazoles between the internal and terminal nickel ions, and we report here its crystal structure and magnetic properties in order to compare them to those of $Ni_3(detrH)_6(NCS)_6{\cdot}2H_2O$.

Experimental Section

Materials. Nickel(II) thiocyanate was prepared as reported in the literature.[9] 3,5-Diamino-1,2,4-triazole (guanazole) was used as the commercially available compound.

Synthesis. The metal salt (1 mmol) dissolved in water (20 mL) was added to the ligand (3 mmol) dissolved in water (6 mL). A very slow evaporation gives blue crystals suitable for X-ray data collection.

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Table I. Crystallographic Data for $Ni_3(SCN)_6(guanazole)_6{\cdot}6H_2O$

$C_{18}H_{42}Ni_3N_{36}O_6S_6$	fw 1227.24
a = 10.448 (2) Å	space group: $R\bar{3}$ (C_{3i}^2, No. 148)
α = 99.81 (1)°	T = 25 °C
V = 1083.93 Å^3	λ = 0.71069 Å
Z = 1	ρ_{obsd} = 1.89 g cm^{-3}; ρ_{calcd} = 1.88 g cm^{-3}
$R(F_o)$ = 0.035	μ = 15.8 cm^{-1}
$R(F_o)^2$ = 0.038	transm coeff = 1.00–0.94

Table II. Final Positional Parameters for $Ni_3(SCN)_6(DAT)_6{\cdot}6H_2O$

atom	x/a	y/b	z/c
Ni(1)	0.5	0.5	0.5
Ni(2)	0.76071 (5)	0.76071 (5)	0.76071 (5)
N(1)	0.2994 (3)	0.5143 (3)	0.4363 (3)
N(2)	0.2006 (3)	0.4114 (3)	0.3472 (3)
N(3)	0.1063 (3)	0.5724 (3)	0.4209 (3)
N(4)	0.2901 (4)	0.7287 (3)	0.5572 (3)
N(5)	−0.0344 (3)	0.3811 (4)	0.2749 (4)
C(1)	0.2364 (3)	0.6075 (3)	0.4760 (3)
C(2)	0.0885 (4)	0.4513 (4)	0.3418 (4)
O(1)	0.4568 (3)	0.9452 (4)	0.7505 (4)
N(6)	0.8781 (3)	0.7302 (3)	0.9323 (3)
C(3)	0.9470 (5)	0.7282 (5)	1.0297 (5)
S(1)	1.0380 (2)	0.7083 (2)	1.1664 (1)

Anal. Calcd for $C_{18}H_{42}Ni_3N_{36}O_6S_6$: C, 17.62; H, 3.45; N, 41.09; S, 15.68. Found: C, 17.53; H, 3.48; N, 41.12; S, 15.65. Carbon, hydrogen, nitrogen, and sulfur were determined with a Carlo Erba 1106 elemental analyzer.

Spectral Measurements. The IR spectra were recorded in the solid state with a Bruker 113r FT-IR spectrophotometer. The spectra in the 4000–400-cm^{-1} range were measured in KBr disks; those in the 400–50-cm^{-1} range were measured in polyethylene disks. Atmospheric water was removed by flushing with dry nitrogen.

Magnetic Susceptibility Measurements. Magnetic susceptibilities were measured in the range 4.2–300 K with a fully automatized AZTEC DSM5 susceptometer equipped with an Oxford Instruments CF 1200S continuous-flow cryostat and a Bruker BE15 electromagnet, operating at ca. 1.2 T. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

X-ray Structure Determination. The intensity data were collected at room temperature on a CAD 4 Enraf-Nonius automatic diffractometer. The crystals were shaped as irregular prisms. Details on crystal data, intensity collection, and structure refinement are reported in Table I. All data were corrected for Lorenz and polarization effects, and an empirical absorption correction, based on the Ψ scan, was applied.[10]

The structure was solved by Patterson and Fourier methods, and refined by full-matrix least-squares calculations, with $\sum_w(|F_o - F_c|)^2$ being minimized. Non-hydrogen atoms were treated anisotropically, whereas the hydrogen atoms were treated as fixed contributors at found positions assuming a temperature factor 1 Å^2 greater than that of the attached nitrogen atoms.

This model converged to R = 0.035 and R_w = 0.038, $w = 1.5/[\sigma^2(F) + 0.0003F_o^2]$. Complex neutral-atom scattering factors[11] were employed throughout; major calculations were carried out on a Vax 11/750 computer, using the SHELX 76[12] program package and the ORTEP[13] plotting program. Final fractional coordinates for nonhydrogen atoms are given in Table II. Bond distances and bond angles are given in Table III.

Results and Discussion

Crystal Structure. The structure of $Ni_3(SCN)_6(guanazole)_6{\cdot}6H_2O$ consists of discrete trimeric, centrosymmetric, complex molecules (Figure 1) and hydrogen-bonded lattice water molecules.

The two crystallographically independent nickel atoms are in special positions, so that the coordination polyhedra have crystallographic imposed symmetries ($\bar{3}$ and 3, respectively), and slightly distorted octahedral coordination geometries.

Table III. Bond Distances (Å) and Bond Angles (deg) with Esd's in Parentheses[a]

Ni(1)–N(1)	2.127 (3)	Ni(2)–N(2)	2.093 (3)	Ni(2)–N(6)	2.097 (4)
N(1)–N(2)	1.429 (4)	C(1)–N(1)	1.314 (5)	C(2)–N(2)	1.304 (5)
C(1)–N(3)	1.343 (5)	C(2)–N(3)	1.352 (6)	C(1)–N(4)	1.366 (5)
C(2)–N(5)	1.369 (5)	C(3)–N(6)	1.149 (6)	C(3)–S(1)	1.641 (6)

N(1)–Ni(1)–N(1)″	90.1 (1)	N(1)–Ni(1)–N(1)‴	89.9 (1)
N(2)′–Ni(2)–N(2)‴	91.1 (1)	N(2)′–Ni(2)–N(6)	89.6 (1)
N(2)⁗–Ni(2)–N(6)	176.9 (1)	N(2)‴–Ni(2)–N(6)	91.9 (1)
N(2)–Ni(2)–N(6)″	87.4 (1)		
N(2)–N(1)–Ni(1)	124.4 (2)	C(1)–N(1)–Ni(1)	129.7 (3)
C(1)–N(1)–N(2)	105.6 (3)	N(1)–N(2)–Ni(2)	124.6 (2)
C(2)–N(2)–Ni(2)	128.7 (3)	C(2)–N(2)–N(1)	106.6 (3)
C(2)–N(3)–C(1)	106.1 (3)	N(3)–C(1)–N(1)	111.1 (3)
N(4)–C(1)–N(1)	127.4 (4)	N(4)–C(1)–N(3)	121.5 (4)
N(3)–C(2)–N(2)	110.7 (3)	N(5)–C(2)–N(2)	127.0 (4)
N(5)–C(2)–N(3)	122.2 (4)	S(1)–C(3)–N(6)	173.8 (5)

[a] Primed atoms are related to unprimed by the following symmetry transformations: X′ = 1 − x, 1 − y, 1 − z; X″ = y, z, x; X‴ = 1 − y, 1 − z, 1 − x; X⁗ = 1 − z, 1 − x, 1 − y of reference coordinates.

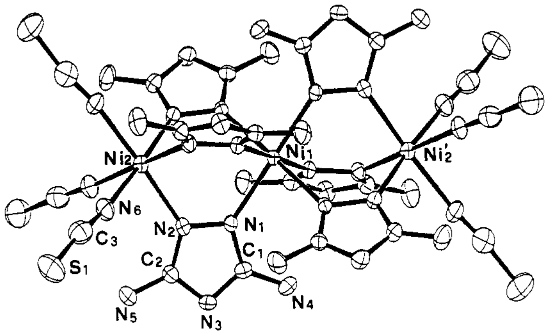

Figure 1. ORTEP view of the complex showing the atom numbering and thermal motion ellipsoids (30%) for the non-hydrogen atoms. The hydrogen atoms are not represented for clarity.

The central nickel atom is coordinated by six N(guanazole) atoms while the terminal nickel atoms are coordinated by three N(guanazole) atoms and three N atoms of the thiocyanate groups.

The two unique Ni–N(guanazole) bond distances (2.127 (3) and 2.093 (3) Å, respectively) are significantly different from each other, and the bond lengthening around the central Ni atom may be influenced to some extent by the crystal packing of six bulky ligand molecules. The Ni–N distances are very close to those found in the literature: 2.052 (3)–2.112 (3) Å in $[(H_2O)_3(C_2H_3N_3)_3Ni]_2(NO_3)_6(H_2O)_2]$[6] and 2.10 (1) Å in $Ni_3(detrH)_6(NCS)_6{\cdot}2H_2O$.[9]

The distortion from ideal octahedral geometry of the coordination polyhedra involve solely the bond angles, whose deviations from ideal values are larger around the terminal Ni atoms (maximum 3.1°), than those around the central metal atom (only 0.1°).

The nickel atoms are displaced from the mean plane through the triazole rings 0.185 and 0.123 Å apart.

The nearest-neighbor Ni–Ni distance within the trimeric molecule is 3.831 (3) Å, longer than that of 3.39 (1) Å observed in $Ni_3(detrH)_6(NCS)_6{\cdot}2H_2O$ and 3.737 (3) Å observed in $[(H_2O)_3(C_2H_3N_3)_3Ni]_2(NO_3)_6(H_2O)_2]$. The triazole rings are found to be planar within experimental error. Bond distances and angles of the ring compare well with those found by other authors.[6,8] The dihedral angles between ring planes are 60.6°.

The terminal NCS groups are N-bonded, and the Ni–N–C angle is 172.6 (5)°.[14] Intermolecular hydrogen-bond contacts, on which the crystal packing mainly depends, occur between the NH_2 of a 2,5-diaminotriazole molecule and water molcules and the S atom of the NCS group.

Vibration Spectra. The fact that the SCN groups are coordinated by the nitrogen atoms as monodentate ligand and that the above groups are cis to each other is well detected in the IR

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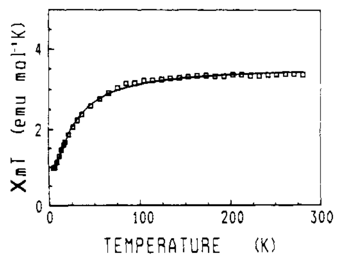
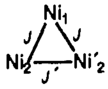


Figure 2. Temperature dependence of χ_mT. The molar magnetic susceptibility is referred to three nickel(II) ions. The solid line represents the best fit (see text).

spectra by the doublet at 2092 and 2106 cm^{-1}. In the far-IR spectrum, four new bands with respect to the free ligand molecule spectrum are found at 343, 318, 253, and 229 cm^{-1}. The bands below 300 cm^{-1} can be assigned to a large contribution of the Ni–N(thiocyanate) stretching modes.[15]

Magnetic Properties. The effective magnetic moments of $Ni_3(guanazole)_6(NCS)_6{\cdot}6H_2O$ are temperature dependent as shown by the χ_mT vs T plot of Figure 2.

In particular, χ_mT decreases with decreasing temperature, indicating a dominating antiferromagnetic coupling between the spins. The experimental data were fitted with the standard expression valid for trinuclear species.[16,17] The input parameters are the g values of the terminal and internal nickel(II) ions, respectively, and the coupling constants defined by



The best fit values are J = 9.32 (5) cm^{-1}, J' = 3.4 (1) cm^{-1}, g_1 = 2.27 (2), and g_2 = 2.16 (1). We use the spin Hamiltonian in the form $H = J\mathbf{S}_1{\cdot}\mathbf{S}_2$. As is usual in trinuclear complexes, the value of J' can be determined with only limited accuracy.[18,19] If J' is fixed at zero, then J is calculated as 10.32 (3) cm^{-1}. Reasonable equivalent fits can be obtained also introducing small zero-field splitting of the ground triplet state. The value of J remains practically constant also in this case. The most reliable parameter that emerges from the analysis is the coupling between the internal and terminal ions, which is weak antiferromagnetic. The extent of the coupling, mediated by the triazole group, is fairly small, if we compare it with the value observed for instance in copper(II) triazolate complexes,[20] where values as large as 204–236 cm^{-1} have been observed. Beyond the difference due to the charged nature of the triazolates, which yield stronger interaction between the metal ions, the reason for this weak coupling must be that the triazolate planes are not parallel to those of the magnetic orbitals of the nickel ions. In fact in this geometry the overlap between the $x^2 - y^2$ and z^2 orbitals of terminal ions and the lone pair of the nitrogen atoms is smaller than in the copper complexes, where the $x^2 - y^2$ orbitals and the triazolates are coplanar. Similar arguments were used also for the mechanism of coupling through imidazolates.[21-23] The difference in the magnetic coupling between $Ni_3(detrH)_6(NCS)_6{\cdot}2H_2O$, which is weak ferromagnetic, and $Ni_3(guanazole)_6(NCS)_6{\cdot}6H_2O$, which is weak antiferromagnetic, must depend on the difference in structure between the two compounds. In fact, for the former two triazoles and one thiocyanate are bridging while for the latter three triazoles are bridging. Therefore, in a simple scheme, the observed difference can be attributed to the substitution of a thiocyanate bridge with one triazole. The weak ferromagnetic coupling in $Ni_3(detrH)_6(NCS)_6{\cdot}2H_2O$ therefore must be the sum of the contributions of two triazoles, which must be antiferromagnetic, and one thiocyanate, which must be ferromagnetic. This kind of coupling has already been observed in copper(II) dimers bridged by azide and isocyanate ions coordinating in an end-on fashion, and has been attributed to spin-polarization effects.[24-28] A similar mechanism might be operative in $Ni_3(detrH)_6(NCS)_6{\cdot}2H_2O$.

Conclusion. Despite the large sterical hindrance, three 3,5-diamino-1,2,4-triazole can be accommodated between two metal ions, yielding tri-μ-bridged structures.

The comparison of the magnetic properties of $Ni_3(guanazole)_6(NCS)_6{\cdot}6H_2O$ and $Ni_3(detrH)_6(NCS)_6{\cdot}2H_2O$ shows that the ferromagnetic coupling observed for the latter is essentially due to the bridging thiocyanate.

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Registry No. $Ni_3(guanazole)_6(NCS)_6{\cdot}6H_2O$, 123774-92-5.

Supplementary Material Available: Tables SI–SV, listing a summary of the intensity data collection, anisotropic thermal parameters, positional and thermal parameters for hydrogen atoms, bond distances and angles involving hydrogen atoms and hydrogen bonding interactions, and selected least-squares planes (5 pages); a table of calculated and observed structure factors (3 pages). Ordering information is given on any current masthead page.

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Contribution from the Departments of Chemistry,
Sogang University, Seoul 121-742, Korea,
and Pusan National University, Pusan 609-735, Korea

Kinetics and Mechanism of the Reactions of a Perchloratorhodium(I) Complex with Nitriles

Chong Shik Chin,[*,†] Sung-Nak Choi,[‡] and Kye-Duck Kim[‡]

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The perchlorato group in $M(ClO_4)(CO)(PPh_3)_2$ (M = Rh, Ir) is so labile that it is readily replaced by various organic molecules (L) to produce cationic metal complexes $[M(L)(CO)(PPh_3)_2]ClO_4$,[1-5] which are catalytically active for the reactions of L.[2-5]

[†] Sogang University.

[‡] Pusan National University.

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