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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, LEHIGH UNIVERSITY,
BETHLEHEM, PENNSYLVANIA 18015, AND MUHLENBERG COLLEGE, ALLENTOWN, PENNSYLVANIA 18104

Preparation and Characterization of Tris(diacetamido)chromium(III) and Tris(dibenzamido)chromium(III)

BY CHARLES S. KRAIHANZEL AND DAVID N. STEHLY

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The new compounds tris(diacetamido)chromium(III), $Cr(C_4H_6O_2N)_3$, and tris(dibenzamido)chromium(III), $Cr(C_{14}H_{10}O_2N)_3$, have been synthesized. Infrared and visible–ultraviolet spectral comparisons suggest that these compounds are structurally analogous to $Cr(acac)_3$ and $Cr(dbm)_3$. The values of *Dq* for the β-diketo and the diamido ligands with Cr(III) are found to be essentially the same. It is concluded that Cr–O π bonding, as it is normally considered to effect *Dq*, cannot be extensive in $Cr(daa)_3$, $Cr(dba)_3$, $Cr(acac)_3$, or $Cr(dbm)_3$.

Introduction

Diacetamide ($CH_3CONHCOCH_3$) and other related amides should be capable of forming metal chelate complexes either in the parent amide form or in the anionic form obtained by removal of the amide hydrogen in a suitable chemical process. This is a property exhibited by only a limited number of ligands, *e.g.*, H_2O and OH^-, NH_3 and NH_2^-. Ionic complexes derived from diacetamide,[1,2] dibenzamide,[3] and other C-alkyl, N-alkyl, and N-phenyl diamides[4] are now known. In 1913, Ley and Werner[5] isolated a compound which analyzed for $Cu(C_6H_5CONCOC_6H_5)_2 \cdot 2H_2O$. To our knowledge this is the only reported neutral transition metal complex derived from a diamide although the nature of attachment of water has not been clearly defined. We wish to report in this paper the syntheses and some physical properties of the new compounds, tris(diacetamido)chromium(III), $Cr(C_4H_6O_2N)_3$, $Cr(daa)_3$, and tris(dibenzamido)chromium(III), $Cr(C_{14}H_{10}O_2N)_3$, $Cr(dba)_3$.

The nature of bonding in these compounds will be discussed in the light of infrared and ultraviolet–visible spectral data. Inasmuch as the diamide, diamido, and β-diketo chelate linkages are isoelectronic and isostructural, the physical properties of these different ligand systems should bear strong relationsips to each other.

Experimental Section

Melting points reported below are uncorrected.

Reagents.—N-Benzoylbenzonitriliumtetrachlorozincate, prepared by the method of Freudenberg,[6] was hydrolyzed over ice and extracted with a saturated solution of sodium bicarbonate to remove residual benzoic acid. The dibenzamide was then extracted from the mixture with 5% sodium hydroxide solution followed by a neutralization of the extract with concentrated hydrochloric acid. The crude product was purified by Soxhlet extraction with diethyl ether to yield a colorless solid (mp 147–148.5°). Diacetamide was prepared by the method of Durrell, Young, and Dresdner[7] and purified by vacuum distillation (mp 78–80°).

Anhydrous chromium(III) chloride was prepared in the laboratory.[8] Chloroform, *n*-hexane, and diethyl ether were used as received from J. T. Baker Chemical Co. (Baker Analyzed reagent). Benzene (Baker Analyzed reagent) was distilled azeotropically to remove the bulk of the water and then drawn through an 18-in. column of activated alumina as needed. Tetrahydrofuran (Matheson Coleman and Bell) was distilled from calcium hydride and redistilled from lithium aluminum hydride directly into the reaction vessels.

Tris(diacetamido)chromium(III).—A slurry of the sodium salt of diacetamide in 150 ml of tetrahydrofuran was prepared from diacetamide (9.1 g, 0.09 mole) and sodium (2.07 g, 0.09 mole). The mixture was heated at reflux and the extent of reaction was monitored by the collection of evolved hydrogen gas; the reaction time to near completion was about 2 days. Anhydrous chromium(III) chloride (4.75 g, 0.03 mole) was added and the mixture was refluxed under nitrogen for 12 hr. At the end of the reflux period the THF was removed under vacuum and the residue was extracted repeatedly with boiling dry benzene to yield a maroon solution. Unreacted anhydrous chromium(III) chloride (0.35 g) was recovered from the reaction residue. The benzene solution was evaporated under vacuum and the resultant maroon solid was transferred under nitrogen to a sublimation apparatus and sublimed at 100° and a pressure of 0.05 mm. The yield was 1.35 g. The sample was further purified by dissolving in diethyl ether, adding 2 vol. of *n*-hexane, filtering, and chilling the filtrate to obtain maroon crystals (mp 180–180.5°). *Anal.* Calcd for $CrC_{12}H_{18}N_3O_6$: C, 40.91; H, 5.15; N, 11.93. Found: C, 41.16; H, 5.06; N, 12.05.

Tris(dibenzamido)chromium(III).—Dibenzamide (10.2 g, 0.045 mole) was dissolved in THF (100 ml) containing finely divided sodium (1.0 g, 0.045 mole). The solution became red-orange and the reaction was assumed complete with the dis-

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[1] C. S. Kraihanzel and S. C. Grenda, *Inorg. Chem.*, **4**, 1037 (1965).

[2] P. S. Gentile and T. A. Shankoff, *J. Inorg. Nucl. Chem.*, **28**, 1283 (1966), and references cited therein.

[3] S. C. Grenda, Ph.D. Thesis, Lehigh University, 1964.

[4] L. Herman and E. Paniago, unpublished results.

[5] H. Ley and F. Werner, *Ber.*, **46**, 4040 (1913). The formula of this copper compound appears to be given improperly in the reference.

[6] K. Freudenberg, *ibid.*, **89**, 209 (1956).

[7] W. S. Durrell, J. A. Young, and R. D. Dresdner, *J. Org. Chem.*, **28**, 831 (1963).

[8] G. B. Heisig, B. Fawkes, and R. Hedin, *Inorg. Syn.*, **2**, 193 (1946).

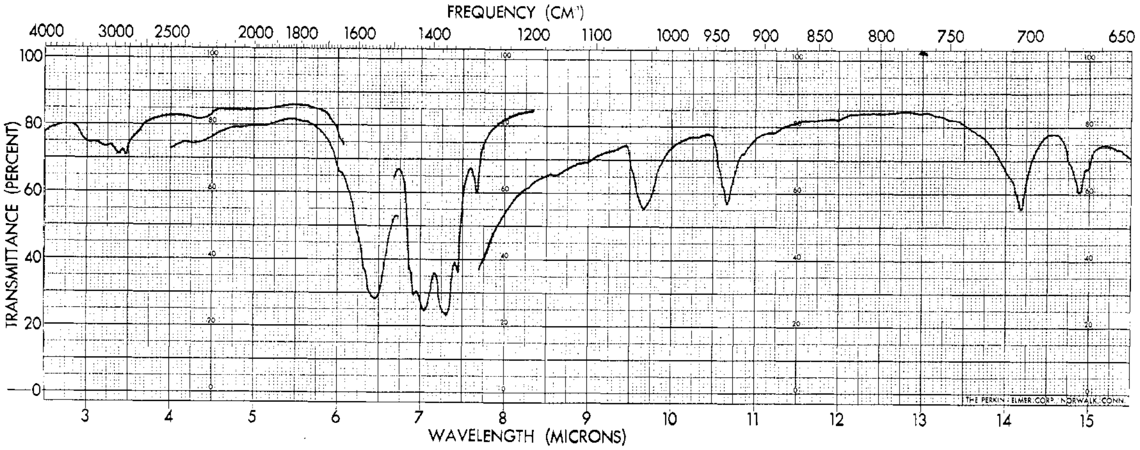

Figure 1.—The infrared spectrum of Cr(daa)$_3$: hexachlorobutadiene mull, 4000–1650 and 1500–1200 cm^{-1}; Nujol mull, 2500–1490 and 1300–650 cm^{-1}.

appearance of the sodium at the end of 1 hr of stirring. Anhydrous chromium(III) chloride (2.00 g, 0.013 mole) was added to the reaction mixture and the system was refluxed under nitrogen for 72 hr. At the end of the reflux period the THF was removed from the reaction mixture under vacuum and the resultant solid was placed in a Soxhlet cup under nitrogen and extracted with dry benzene. The maroon solid was isolated from the benzene solution by evaporation under vacuum. The material was purified using the same technique as in the final purification of the diacetamide complex; yield, 1.55 g (16.9%) (mp 273–274.5°). *Anal.* Calcd for $CrC_{42}H_{30}N_3O_6$: Cr, 7.18; C, 69.61; H, 4.17; N, 5.80. Found: Cr, 7.13; C, 70.00; H, 4.66; N, 5.69.

The compounds tris(acetylacetonato)chromium(III)[9] and tris(dibenzoylmethano)chromium(III)[10] were prepared by methods previously described in the literature.

Spectrophotometric Measurements.—Infrared spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer in the region 600–4000 cm^{-1}. Samples were examined as mulls in Nujol oil and hexachlorobutadiene and as 2% solutions in chloroform. Nujol oil was dried by percolation through anhydrous activated alumina; hexachlorobutadiene was dried by distillation from calcium hydride.

Electronic spectra in the visible and ultraviolet regions were obtained with a Beckman DK-2A quartz prism ratio recording spectrometer. Chloroform and dry benzene were used as solvents.

Susceptibility Measurements.—Magnetic measurements were made with a permanent magnet (4200 gauss) on solid samples in Pyrex tubes which had been calibrated with mercury(II) tetrathiocyanatocobaltate(II) and Mohr's salt.[11]

Results and Discussion

Cr(daa)$_3$.—The compounds Cr(acac)$_3$ and Cr(daa)$_3$ are similar in several respects. Both are deep maroon, quite soluble in nonpolar solvents such as benzene, sublimable at 100° (10^{-2} mm), and fully paramagnetic with μ_{eff} of 3.97 ± 0.10 BM. However, Cr(daa)$_3$ is quite unstable to hydrolysis, whereas Cr(acac)$_3$ is readily prepared in aqueous solution. No doubt, hydrolysis of Cr(daa)$_3$ is initiated by attack of the ligand at nitrogen and/or carbon and not at the metal site. Moist air and undried organic solvents are sufficient to cause formation of green residues which are water soluble but insoluble in nonpolar organic solvents. The formation of these green products causes considerable difficulty in recrystallization.

Cr(dba)$_3$.—The compound Cr(dba)$_3$ is fully paramagnetic (μ_{eff} = 3.99 ± 0.10 BM) and soluble in nonpolar organic solvents. Unlike Cr(dbm)$_3$, which is a gold-brown solid, Cr(dba)$_3$ has the same deep maroon color as Cr(daa)$_3$. Although Cr(dba)$_3$ appeared to be hydrolytically more stable than Cr(daa)$_3$ and can be handled in air for brief periods, storage in a dry atmosphere is necessary.

Infrared Spectra.—A composite-mull infrared spectrum of Cr(daa)$_3$ is shown in Figure 1. The frequencies and suggested assignments are recorded in Table I. These assignments have been made with the aid of those reported earlier for *trans–trans*-diacetamide, various

TABLE I

INFRARED SPECTRA (CM^{-1})[a]

Cr(daa)$_3$	Assignment	*trans–trans* Diacetamide[b]	Assignment
. . .	. . .	3280 s	NH str
		3205 s	
2900 vw	CH str	2960 m	CH str
		2920 m	
1551 s	CO sym str	1734 s	Imide I_s
1449 sh, s	CO asym str	(1695) s	Imide I_a
. . .	. . .	1505 s	Imide II CNC asym str + NH def (ip)
1424 s	CH def	1425 m	CH def
1375 s	CH def	1372 m	CH def
1346 sh, m	CNC asym str	. . .	. . .
1302 w	CNC sym str	1295 w, sh	CNC sym str
. . .	. . .	1236 s	Imide III, NH def (ip) and CNC asym str
1036 m	CH_3 wag	1035 m	CH_3 wag
939 m	CH_3 wag	920 m	CH_3 wag
. . .	. . .	739 m	NH def (op)
707 m			
714 sh	MO str and/or ring def		
674 m			
669 sh			

[a] Hexachlorobutadiene mulls, 4000–1650 and 1500–1200 cm^{-1}; Nujol mulls, 2500–1490 and 1300–650 cm^{-1}. Notations: s, strong; m, medium; w, weak; sh, shoulder. [b] Reference 1.

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[9] W. C. Fernelius and J. E. Blanch, *Inorg. Syn.*, **5**, 130 (1957).

[10] J. P. Collman, R. A. Moss, H. Maltz, and C. C. Heindel, *J. Am. Chem. Soc.*, **83**, 531 (1961).

[11] B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 415.

metal complexes of *trans–trans*-diacetamide,[1] and Cr(acac)$_3$.[12] As has been done in previous studies, we assume that the coupling of ring vibrations through the metal atom is negligible and that a simple model of a single ligand chelated to the metal atom is sufficient.

As expected, Cr(daa)$_3$ exhibits neither NH stretching nor NH out-of-plane deformation modes; these were found *ca.* 3200–3300 and 740–770 cm^{-1}, respectively, in M(daaH)$_3$(ClO$_4$)$_2$ complexes.[1] The coupling of the CNC asymmetric stretch and the NH in-plane deformation found in the charged complexes gave rise to two bands at about 1500 and 1250 cm^{-1}. Each of these modes, if allowed to operate independently, would appear near 1370 cm.$^{-1}$. The CNC asymmetric stretch in N-deuterio-*trans–trans*-diacetamide, for which coupling with the N–D in-plane deformation is minimal, is found at 1348 cm^{-1}.[13] We therefore assign the shoulder at 1346 cm^{-1} in Cr(daa)$_3$ as the CNC asymmetric stretching mode. A similar type of coupling is responsible for the appearance of three to four bands in the region above 1400 cm^{-1} in acetylacetonates as has been discussed by Nakamoto.[12] The separation of about 100 cm^{-1} between the symmetric and asymmetric CO stretching modes of Cr(daa)$_3$ is also reasonable when compared with a separation of 97 cm^{-1} reported for Cr(acac)$_3$. Thus, in contrast to acac complexes for which the highest frequency band in the 1500–1600-cm^{-1} region is best assumed as containing significant C═C character,[12] the highest band in Cr(daa)$_3$ is most likely a carbonyl mode. Although the other vibrational modes may be routinely assigned on the basis of previous assignments in diacetamide and/or Cr(acac)$_3$, we do not consider all of these assignments as final. There appears to be no doubt, however, that the basic structure of Cr(daa)$_3$ is not unlike that of Cr(acac)$_3$.

Electronic Spectra.—The Spectra of the compounds are given in Figure 2. The following discussion is based on the assumption that the approximation of an octahedral field is sufficient for the assignment of d–d transitions. Spectral evidence reported by Jørgensen[14] and the structural parameters of Cr(acac)$_3$ as reported by Morisin[15] indicate that this is a good approximation. On this basis, the bands at 17,800 and 24,250 cm^{-1} for Cr(daa)$_3$ can be assigned as the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ transitions, respectively. These transitions are very close to those observed at 17,400 and 24,500 cm^{-1} for Cr(H$_2$O)$_6^{3+}$.[16] Similarly, the corresponding bands for Cr(acac)$_3$ appear at 17,650 cm^{-1} and as a shoulder centered near 24,100 cm^{-1} on the near-ultraviolet band. A similar assignment was suggested by Barnum.[17]

The *Dq* values found for the complexes Cr(daa)$_3$, Cr(acac)$_3$, and Cr(H$_3$O)$_6^{3+}$ are 1780, 1765, and 1740, respectively, and suggest that the ligand field is not appreciably different for this series of ligands. This trend would seem to be incongruous inasmuch as acac, which is normally considered to be a π-bonding ligand with Cr(III), ought to have a value of *Dq* considerably different from that of water which presumably is incapable of π bonding. However, evidence has been cited for π bonding by acac. Such evidence includes the reduction of the electron repulsion parameters for d–d transitions in Cr(acac)$_3$[18] and the spin delocalization in the acac ligand as measured by nmr contact shifts.[19] Barnum[20] has suggested that this apparent anomaly arises as a consequence of MO π bonding of the d$_\epsilon$ electrons with both the occupied π_3 and unoccupied π_4 orbitals of the ligands. This would result in a further splitting of the π_3 and π_4 levels and would create a third π level of predominantely d character not much different from the original d level in energy. A similar interaction is theoretically possible with the diamide and diamido π systems. On the assumption that the bonding in each case is identical, the energies of a set of Hückel-type molecular orbitals have been calculated for these ligand systems using the parameters listed in Table II.

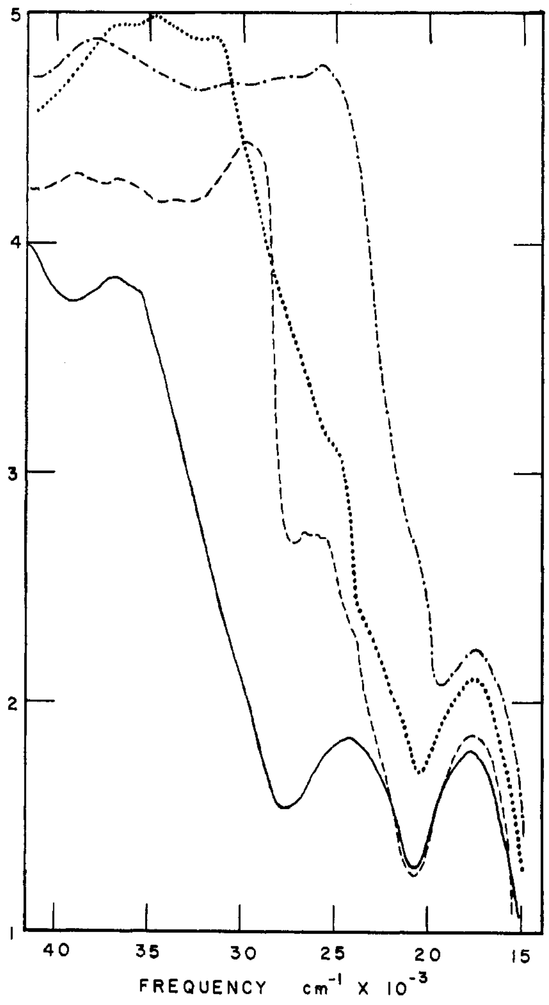

Figure 2.—Visible–ultraviolet spectra in chloroform solutions at 25° and 1.0-cm path length: Cr(daa)$_3$, ———; Cr(acac)$_3$, - - - -; Cr(dba)$_3$, ... ; Cr(dbm)$_3$, — · — ·.

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(12) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 216.

(13) T. Uno and K. Machida, *Bull. Chem. Soc. Japan*, **34**, 551 (1961).

(14) C. K. Jørgensen, *Acta Chem. Scand.*, **16**, 2406 (1962).

(15) B. Morisin, *Acta Cryst.*, **19**, 131 (1965).

(16) C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1495 (1954).

(17) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961).

(18) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **36**, 3330 (1962).

(19) D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).

(20) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **22**, 183 (1961).

The lowest three levels in each case are fully populated. A rough calculation using a value of $\beta_{MO} = 11{,}000$ cm^{-1}, the above-mentioned ligand π-orbital energies, and other data from Barnum's work would indicate that Dq should be on the order of 200 cm^{-1} greater for daa than acac. The observed difference of 15 cm^{-1} is in the correct direction but is not sufficiently large to suggest that strong MO π bonding, extending through the entire ligand π system, need be invoked to rationalize the values of Dq. This suggests that the predominant electronic effect in these compounds is in the σ system, although not necessarily of a simple electrostatic nature.

Table II

Energies of π Molecular Orbitals in O–C–X–C–O Compounds[a]

	X = CH	X = N:	X = N–H
π_5	−1.574	−1.089	−0.927
π_4	−0.505	−0.505	−0.505
π_3	+0.712	+0.929	+1.234
π_2	1.605	1.605	1.605
π_1	1.961	1.959	2.293

[a] Parameters: $\alpha_C = \alpha$; $\alpha_O = \alpha + 1.1\beta$; $\alpha_{N:} = \alpha + 0.7\beta$; $\alpha_{NH} = \alpha + 1.5\beta$; $\beta_{CC} = \beta$; $\beta_{CO} = 0.9\beta$; $\beta_{CN} = 0.8\beta$.

In spite of the crudeness of the Hückel approximation used in calculating the energies of the π levels of the ligands, they would seem to be qualitatively correct. The lowest energy ligand–ligand transition which is allowed in each case should correspond to the $\pi_3 \rightarrow \pi_4$ transition. From the spectra, it is obvious that the lowest energy allowed transition for $Cr(daa)_3$ appears near 36,000 cm^{-1} (doublet with maxima at 35,500 and 37,000 cm^{-1}) compared to 29,650 cm^{-1} for $Cr(acac)_3$.[21] The ratio of these frequencies is 1.21 which compares very favorably with the predicted ratio of 1.18. The corresponding $\pi_3 \rightarrow \pi_4$ transition for diacetamide would then be expected near 43,200 cm^{-1} and no intense transition is noted below 42,000 cm^{-1} for this compound in chloroform.

A similar comparison may be made for $Cr(dbm)_3$ and $Cr(dba)_3$. The respective ligand field transitions at 17,600 and 17,750 cm^{-1} indicate that the substitution of phenyl for methyl lowers Dq slightly in each case. This is expected inasmuch as the inductive withdrawal of electronic charge by phenyl compared to methyl would lower the relative charge buildup on oxygen and thus provide a weaker ligand field. The relative energies of the ligand–ligand transitions also account for the distinctly different colors of the dbm and dba complexes. Conjugation of each of the ligand π systems with phenyl rings ought to shift the allowed $\pi \rightarrow \pi^*$ transitions to considerably lower energy compared to the methyl analogs. In fact, the lowest energy $\pi \rightarrow \pi^*$ transition at 25,850 cm^{-1} for $Cr(dbm)_3$ extends into the visible and thus imparts a gold-brown color to this solid. The first intense transition for $Cr(dba)_3$ (maximum at 31,700 cm^{-1}; other maxima at 34,650 and 36,900 cm^{-1}) is still fully contained in the ultraviolet region and as such does not influence the color of the solid which is identical with that of $Cr(daa)_3$.

Acknowledgment.—The award of a Lutheran Church in America Education Fund Faculty Summer Study Grant to David N. Stehly during the course of this work is gratefully acknowledged.

[21] K. DeArmond and L. S. Forster, *Spectrochim. Acta*, **19**, 1393 (1963). These authors have demonstrated that this band and the other ultraviolet bands of $Cr(acac)_3$ are most likely $\pi \rightarrow \pi^*$ transitions and not charge transfer in origin.

Contribution from Centro Composti di Coordinazione C.N.R.,
Istituto di Chimica Generale ed Inorganica, Università di Padova, Padua, Italy

Reactivity of Amines toward Cationic Gold(III) Complexes

By L. CATTALINI, A. DONI, and A. ORIO

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The influence of basicity upon the reactivity of substituted pyridines toward $[AuCl_4]^-$ does not change in going from methanol to acetone as solvent. The role of basicity in determining the nucleophilicity of the entering groups becomes greater when unipositive gold(III) complexes are used as substrates, and the nature of the groups bonded to the metal appears to affect strongly the relationship between the basicity and the reactivity.

Introduction

Some studies on the relationship between the reactivity of square-planar platinum(II) and gold(III) complexes and the properties of amines acting as either entering or leaving groups have been recently published.[1–3] Although "softness" is the most important factor in determining the nucleophilicity of reagents toward Pt(II) substrates, it has been observed[2] that the "softness" of the amines, as felt by Pt(II), is not significantly affected by the nature of the groups attached to the nitrogen so that, in the replacement of the chloride in $[Pt(bipy)Cl_2]$ by amines, it was possible to study the dependence of reactivity upon the basicity of the entering group. As expected, in the neutral Pt(II) complex the soft substrate cannot discriminate

[1] L. Cattalini and M. L. Tobe, *Inorg. Chem.*, **5**, 1145 (1966).

[2] L. Cattalini, A. Orio, and A. Doni, *ibid.*, **5**, 1517 (1966).

[3] L. Cattalini, M. Nicolini, and A. Orio, *ibid.*, **5**, 1674 (1966).