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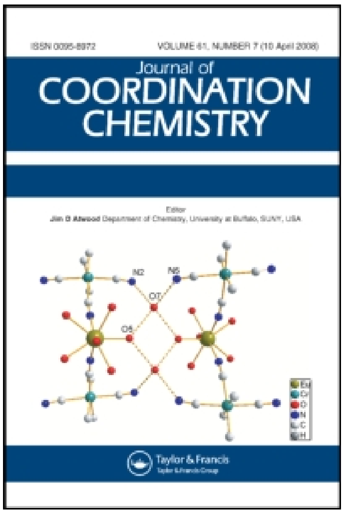

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Stocco, G. C. , Gattuso, F. Stocco , Bertazzi, N. and Pellerito, L.(1976) 'SYNTHESIS, LASER-RAMAN, INFRARED AND PROTON MAGNETIC RESONANCE SPECTRA OF $(CH_3)_3PtX^{2-}_3$ IONS ($X = Cl^-, Br^-$) AND $(CH_3)_3Pt^{iv}$ ISOCYANIDE COMPLEXES', Journal of Coordination Chemistry, 5: 2, 55 — 60

To link to this Article: DOI: 10.1080/00958977608075921

URL: http://dx.doi.org/10.1080/00958977608075921

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J. Coord. Chem.
1976, Vol. 5, pp. 55–60

SYNTHESIS, LASER-RAMAN, INFRARED AND PROTON MAGNETIC RESONANCE SPECTRA OF $(CH_3)_3PtX_3^{2-}$ IONS ($X = Cl^-, Br^-$) AND $(CH_3)_3Pt^{IV}$ ISOCYANIDE COMPLEXES

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(*Received March 3, 1975; in final form May 28, 1975*)

The novel ionic complexes $[(C_6H_5)_4As]_2\,[(CH_3)_3PtX_3]$ ($X = Cl^-$ and Br^-) and $[(CH_3)_3Pt(bipy)L]^+[B(C_6H_5)_4]^-$ (bipy = 2,2′-bipyridine, L = aliphatic and aromatic isocyanide) have been prepared. The structure of the complex ions has been inferred from Laser–Raman and infrared spectra in the solid state and ^1H NMR in solution. These data are consistent with a facial configuration of the organometallic moiety. Trends in vibrational frequencies ν(Pt–C) and ν(Pt–X) indicate a "trans" influence sequence for the ligands, which in the case of $(CH_3)_3PtX_3^{2-}$ is related with that found for $(CH_3)_2AuX_2^-$ ions.

INTRODUCTION

The trimethylplatinum(IV) moiety forms a number of stable ionic complexes with monodentate ligands. Complexes of the type $[(CH_3)_3PtL_3]^+$ [L = neutral monodentate ligand as ammonia,[1,2] substituted phosphines[3]] as well as mixed derivatives of the type $[(CH_3)_3PtL'_2L'']^+$ have been reported.[3,4] They have been investigated by NMR and vibrational spectroscopies; and orders of "*trans*" influence for the various groups bound to platinum(IV), based essentially on (Pt–C) stretching frequencies and NMR coupling constants, have been advanced. The different characteristics of pyridine and ammonia are reflected in the formation of the $[(CH_3)_3Pt(NH_3)_3]^+$ ion by dissolving $[(CH_3)_3PtI]_4$ in liquid ammonia, while the neutral species $(CH_3)_3Ptpy_2I$ was obtained when trimethylplatinum(IV) iodide was dissolved in pyridine.[2] Anionic $(CH_3)_3PtX_3^{2-}$ species have also been reported[5] in a PMR and Raman study of solutions obtained dissolving $[(CH_3)_3Pt]_2SO_4.4H_2O$ in water containing excess of CN^- and SCN^- ions.

In this communication we report the synthesis, infrared and Raman spectra of solid $(CH_3)_3PtX_3^{2-}$ ($X = Cl^-$ and Br^-) anionic complexes and of cationic complexes $[(CH_3)_3Pt\ bipy\ L]^+$ [bipy = 2,2′-bipyridine; L = cyclohexyl – and o-tolylisocyanide, not included in the series of compounds above mentioned[3]]. The nature of solutions of the complexes has been investigated by conductivity and PMR spectra.

EXPERIMENTAL

The starting material $[(CH_3)_3PtI]_4$ was prepared by the method of Clegg and Hall.[6]

The chloride and the bromide were obtained from the iodide by a metathetical reaction analogous to that of dimethylgold(III) halides.[7] Tetraphenylarsonium chloride was purchased from Fluka (Switzerland) and used without purification. The bromide (iodide) was prepared by addition of an aqueous solution of KBr(KI) to $(C_6H_5)_4AsCl$ dissolved in ethanol.

The synthesis of $[(C_6H_5)_4As]_2[(CH_3)_3PtX_3]$ ($X = Cl^-$ and Br^-) was effected by dissolving in chloroform under reflux 2 m moles of $(C_6H_5)_4AsX$ ($X = Cl^-$ or Br^-) and 1 m mole of the corresponding trimethylplatinum(IV) halide. The solution was filtered, reduced to *ca.* 10 ml on a rotary evaporator and cooled. The white crystals which precipitated were filtered and dried over P_4O_{10}. Following the same procedure outlined above, the iodide derivative was obtained in solution, and PMR spectra were taken. The isocyanide complexes have been prepared following a route similar to that reported in ref. (3). Microanalyses were performed by Laboratorio di Microanalisi, Istituto di Chimica Farmaceutica (Padova) and are reported in Table I.

Proton magnetic resonance spectra were recorded with Varian XL-100 and Jeol C60 spectrometers, with the probe temperature approximately 40° and 26°, respectively. Conductivity measurements were

TABLE I

Analytical data [found (calcd.) %], melting points (decomp.), °C, and molar conductivity in nitromethane at 26°C (Ω^{-1} cm^2 mole^{-1}) of trimethylplatinum(IV) complexes

Compound	M.p.	C	H	X	Pt	Concn. M (x 10^3)	M[a] (Ω^{-1} cm^2 mol
$[(C_6H_5)_4As]_2[(CH_3)_3PtCl_3]$	198	55.70	4.77	9.37	17.07	1	139.9
		(55.01)	(4.40)	(9.52)	(17.52)	0.6	140.4
$[(C_6H_5)_4As]_2[(CH_3)_3PtBr_3]$	200	48.81	4.13	18.96	16.18	1	143.1
		(49.12)	(3.93)	(19.26)	(15.67)	0.6	150.4
$[(CH_3)_3Pt(bipy)^bC_6H_{11}NC]^+[B(C_6H_5)_4]^{-c}$	120	64.09	5.68	5.03[d]		4.94	58.74
		(64.07)	(5.87)	(5.09)		1.73	62.77
						0.49	65.65
$[(CH_3)_3Pt(bipy)^b o\text{-}CH_3C_6H_4NC][B(C_6H_5)_4]^{-c}$	140	64.68	5.19	4.90[d]		7.63	50.47
		(64.89)	(5.34)	(5.05)		2.67	55.99
						0.53	61.18

[a] $(C_6H_5)_4AsCl$, Λ_M(conc., M x 10^3): 87.7(1.2); 88.3(0.6)
[b] bipy = 2,2′-bipiridine
[c] $[(C_4H_9)_NN]^+[B(C_6H_5)_4]^-$, Λ_M (conc., M x 10^3): 61.65(1.10) (see reference 8)
[d] X = Nitrogen.

TABLE II

PMR spectra (TMS internal standard) of trimethylplatinum(IV) complexes

	Methyl "trans" to Bipy		Methyl "trans" to L[a]	
Compound	$\tau(CH_3)$, ppm	$^2J(^{195}Pt{-}C{-}^1H)$, Hz	$\tau(CH_3)$, ppm	$^2J(^{135}Pt{-}C{-}^1H)$, Hz
$[(CH_3)_3Pt(bipy)C_6H_{11}NC]^+[B(C_6H_5)_4]^-$	8.75[b]	69.0	9.72[b]	60.0
	8.78[c]	69.0	9.72[c]	60.0
$[(CH_3)_3Pt(bipy)o\text{-}CH_3C_6H_4NC]^+[B(C_6H_5)_4]^-$	8.70[c]	68.2	9.12	71.2
$[(C_6H_5)_4As]_2[(CH_3)_3PtCl_3]$				
$[(C_6H_5)_4As]_2[(CH_3)_3PtBr_3]$				
$[(C_6H_5)_4As]_2[(CH_3)_3PtI_3]^h$				
$[(CH_3)_3PtCl]_4$				
$[(CH_3)_3PtBr]_4$				
$[(CH_3)_3PtI]_4$				

Compound	$\tau(CH_3)$, ppm[g]	$^2J(^{195}Pt{-}C{-}^1H)$, Hz	Other signals[d]
$[(CH_3)_3Pt(bipy)C_6H_{11}NC]^+[B(C_6H_5)_4]^-$			6.15[c] 8.55 8.63[bd]
$[(CH_3)_3Pt(bipy)o\text{-}CH_3C_6H_4NC]^+[B(C_6H_5)_4]^-$			7.90
$[(C_6H_5)_4As]_2[(CH_3)_3PtCl_3]$	8.75	80.9	
$[(C_6H_5)_4As]_2[(CH_3)_3PtBr_3]$	8.52	80.5	
$[(C_6H_5)_4As]_2[(CH_3)_3PtI_3]^h$	8.15	80.2	
$[(CH_3)_3PtCl]_4$	8.58[e]	81.7[e]	
$[(CH_3)_3PtBr]_4$	8.46[e]	80.1[e]	
$[(CH_3)_3PtI]_4$	8.27[e]	78.4[e]	
	8.27[f]	78.6[f]	

[a] L = notation referred to the general formula $[(CH_3)_3Pt(bipy)L]^+$ of the complexes.
[b] Solvent: $(CD_3)_2CO$.
[c] Solvent: CD_2Cl_2.
[d] Aromatics: τ 2.0–3.5. Abbreviations: bd = broad.
[e] See reference 9.
[f] Solvent: $CDCl_3$.
[g] Aromatics: τ 2.0–2.5
[h] Not isolated as a solid. The solution was obtained dissolving trimethylplatinum(IV) and tetraphenylarsonium iodide in 1:2 molar ratio.

determined with a LKB conductolyzer type 5300 B. Infrared spectra were recorded on Perkin Elmer 225 and 457 spectrometers as split mulls. Instrument calibration was effected with polystyrene films. Far-infrared spectra were run as nujol mulls between polyethylene windows on a Beckman IR–11 spectrometer. The frequencies for sharp bands are accurate to ±2 cm^{-1} while those for broad bands should be within ±5 cm^{-1}. For these spectra we are indebted to Prof. S. Califano (University of Florence) and Prof. C. Pecile (University of Padua). Raman spectra of $(CH_3)_3PtX_3^{2-}$ complexes were obtained with a Cary 83 Laser–Raman spectrometer by courtesy of Varian Italiana during the 1972 Laser–Raman Workshop in Rome. He–Ne excitation was used (6328 Å). Raman spectra of isocyanide complexes were measured with the assistance of Prof. J. Brandmüller (Institute of Physics, University of Munich). The spectra have been excited with a Spectra Physics Mod. 165 krypton laser at 6471 Å and recorded with an RSV 1 -m double monochromator, a thermo-electrically cooled RCA C 31000 E photomultiplier and photon counting detection. With 6471 Å krypton laser excitation we had to lower the laser power to about 300 mw for the o-tolylisocyanide complex and to 150 mw for the cyclohexylisocyanide complex respectively, in order to prevent decomposition of the sample. To the same purpose the rotating Raman sample technique was employed.[10] Calibration of the monochromator was effected with the exciting line and background plasma lines and chloroform. The frequencies for sharp lines are accurate to within ±5 cm^{-1} while those for broad bands should be within ±10 cm^{-1}. A strong fluorescence was exhibited by all the compounds. The samples were sealed in capillary tubes, and the trans-illumination technique was employed. Solution spectra were obtained, with nearly saturated solutions in $CHCl_3$, using a 2.5 ml Perkin Elmer multi-reflection cell.

RESULTS

Proton Magnetic Resonance Spectra

PMR spectra relative to the organometallic moiety of the isocyanide complexes are characterized by two signals with intensity ratios 2:1, flanked by satellites due to $^2J(^{195}Pt{-}C^1H)$. The PMR spectra of the $(CH_3)_3PtX_3^{2-}$ complexes show a single peak due to magnetically equivalent methyl groups bound to platinum, flanked by satellites. These features are common with the parent halides spectra, which are also reported (Table II). An attempt was made to investigate whether a halide exchange process was present in solutions of the halide complexes but whenever equimolar solutions in $CDCl_3$ of $[(C_6H_5)_4As]_2\,[(CH_3)_3PtCl_3]$ and $[(C_6H_5)_4As]_2\,[(CH_3)_3PtBr_3]$ were mixed, a precipitate appeared which was found to be a mixture of $(C_6H_5)_4AsCl$ and $(C_6H_5)_4AsBr$.

Raman and Infrared Spectra

In Table III the most significant frequencies for isocyanide complexes are reported. From the Raman and infrared spectra, the vibrations associated with the complex anions $(CH_3)_3PtCl_3^{2-}$ and $(CH_3)_3PtBr_3^{2-}$ have been assigned, and they are tabulated in Table IV. The assignments of the frequencies were made by analogy with the spectra of the trimethylplatinum halides.[11,12] Vibrations of the $(C_6H_5)_4As^+$ cation were identified from Raman and infrared spectra of the corresponding chloride and bromide and the literature values.[13] The compounds were strongly fluorescent both as crystalline powders and as chloroform solutions. The powder and solution Raman spectra for $(CH_3)_3PrBr_3^{2-}$ for the ν(Pt–C) region are shown in Fig. 1.

DISCUSSION

Conductivity data (Table 1) suggest that the isocyanide and the halide complexes in nitromethane

TABLE III
Laser–Raman and infrared data for trimethylplatinum(IV) isocyanide complexes (ν, cm^{-1})

	$\nu(PtC_3)$	ν(NC)		
	(Raman)	Raman	i.r.	$\Delta\nu(NC)^a$
$[(CH_3)_3Pt(bipy)C_6H_{11}NC]^+[B(C_6H_5)_4]^-$	576	2247	2240	102
$[(CH_3)_3Pt(bipy)o\text{-}CH_3C_6H_4NC]^+[B(C_6H_5)_4]^-$	569 580 597	2189	2195	73

$^a\Delta\nu(NC) = [\nu(NC)(complex)] - [\nu(NC)(free\ ligand)]$

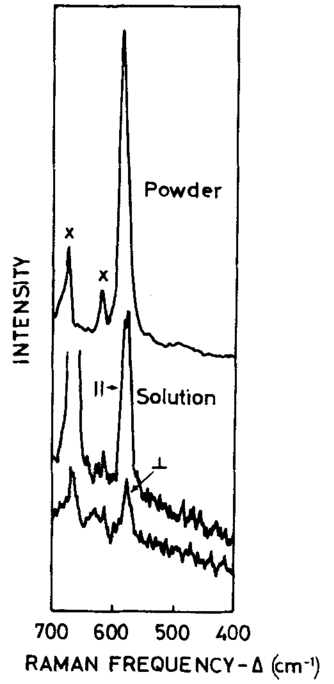

FIGURE 1 Laser Raman spectra of $(CH_3)_3PtBr_3^{2-}$. The spectra were recorded with microcrystalline powders and chloroform solutions. Grating ghosts and scattering from the $(C_6H_5)_4As^+$ ion are marked with X.

solution are 1:1 and 2:1 electrolytes respectively.[14] The PMR spectra of the anions are consistent with the existence of $(CH_3)_3PtX_3^{2-}$ species with methyl groups in a *facial* configuration. A *meridional* configuration is ruled out as two sets of methyl resonances with different coupling constants are expected on this basis. The similarity between $(CH_3)_3Pt^{IV}$ and $(CH_3)_2Au^{III}$ moieties has been previously outlined.[15] The trimethylplatinum(IV) derivatives, in general, appear to be more inert than dimethylgold(III) compounds. An equimolar solution of trimethylplatinum chloride and iodide in $CHCl_3$ at 58° did not show an exchange process such as has been found for mixtures of dimethylgold(III) halides.[16] The $^2J(^{195}Pt{-}C{-}^1H)$ coupling constants have been found to depend on the nature of the "trans" ligand in several organo Pt^{II} and organo Pt^{IV} derivatives.[17] In these complexes (Table II) as well as in the parent halides, $^2J(^{195}(Pt{-}C{-}^1H)$ decreases in going from the chloro to the iodo-derivative, suggesting a reverse "trans" influence order of the halides which parallels their polarizability. A similar trend is shown both by the halides and the complexes for the methyl proton resonances, which consistently shift to lower field as the "trans" halide becomes more polarizable. The vibrational frequencies and the coupling constant $^2J(^{195}Pt{-}C{-}^1H)$ for the platinum–methyl groups

TABLE IV
Infrared and Laser–Raman (He–Ne) spectra of $(CH_3)_3PtX_3^{2-}$ complexes (ν, cm^{-1})[a]

$[(C_6H_5)_4As]_2[(CH_3)_3PtCl_3]$		$[(C_6H_5)_4As]_2[(CH_3)_3PtBr_3]$			Qualitative assignments
			Raman		
I.r.	Raman(powd.)[b]	I.r.	powd.[b]	$CHCl_3$ soln	Qualitative assignments
		136 w			ν(Pt–Br)
		151 m			
		172 m			
212 m					ν(Pt–Cl)
282 w, bd		288 w, bd			$\delta(PtC_3)$
c	585 vs, sh[d]	c	569 vs, sh[d]	573 p 565 vs	ν(Pt–C)
1225 m, sh	1225 m	1220 m, sd	1220 m	1210 m	$\delta_s(CH_3)$
1260 w		1225 m			
2810 m		2820 m			$2x\delta_{as}(CH_3)$
2906 s, sh	2920 m	2920 s, sh	2935 m	2930 m	$\nu_s(CH_3)$
2980 m		2980 m			$\nu_{as}(CH_3)$

[a] Frequencies due to $(C_6H_5)_4As^+$ have not been tabulated. Abbreviations: w = weak, m = medium, s = strong, v = very, sh = sharp, sd = shoulder, p = polarized.
[b] Scan speed = 6 cm^{-1}/sec; slit width = 4 cm^{-1}.
[c] ν(Pt–C) vibrations are too weak to be assigned with any confidence.
[d] With this resolution only one Raman line was observed.

may be tentatively used[3] as a measure of the "trans" influence of the ligands "trans" to the platinum methyl group. The skeletal PtC_3 stretching modes are extremely weak in the infrared spectra and could not be identified with any confidence, while they are quite intense in the Raman spectra. The effective symmetry of the trimethylplatinum(IV) isocyanide molecules may be taken as Cs and three Raman active bands are expected in the 500–600 cm^{-1} region, ascribable to the platinum–methyl stretching vibrations. While accidental degeneracy gives rise to only one band (576 cm^{-1}) in the cyclohexylisocyanide complex, the expected three bands (569, 580 and 597 cm^{-1}) are present in the o-tolylisocyanide derivative. The average value for the platinum–methyl stretching frequencies is 582 cm^{-1} for the o-tolylisocyanide complex, compared with 576 cm^{-1} for the cyclohexylisocyanide (Table III) derivative and $^2J(^{195}Pt\text{–}C\text{–}^1H)$ are 71, 2 and 60.0 Hz respectively. Both types of data are consistent in indicating a higher "trans" influence for the cyclohexylisocyanide ligand. In addition, the NC stretching vibrations show an increase of frequency with respect to the free ligand, which is higher for the alkylisocyanide. This is in agreement with a higher positive charge on the platinum atom[3] and with a higher NC bond order for the cyclohexylisocyanide compared with the o-tolyl derivative.

For all trimethylplatinum(IV) compounds whose X-ray structures have been determined, the methyl groups appear to be arranged *in a fac configuration*; accordingly, the structure for the trihalogenotrimethylplatinate(IV) ion which may be advanced is shown in Fig. 2. The skeletal symmetry or the effective symmetry, assuming free rotation of the methyl groups, is C_{3v}, compared to T_d for the parent halides, although the local symmetry around platinum in the halides also is C_{3v}. Only the skeletal modes of the $(CH_3)_3PtX_3^{2-}$ ions will be considered here.

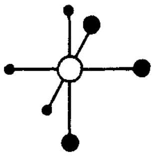

FIGURE 2 Structure of $(CH_3)_3PtX_3^{2-}$ ($X = Cl^-, Br^-$) ions. ○ = Pt; ● = C; ● = X.

The representation for the normal modes is reported in Table V, along with an approximate description of the modes, as no normal coordinate analysis was attempted in view of the paucity of the frequencies observed from infrared and Raman spectra. Many of these skeletal frequencies are also very similar to those $[(CH_3)_3PtX]_4$ parent halides (T_d symmetry) and can be assigned on this basis.

TABLE V
Selection rules for the C_3PtX_3 skeleton

Species and activity	Approximate description of the mode
A_1 (i.r. and R.)	ν_1 Pt–C stretch ν_2 Pt–X stretch ν_3 PtC_3 bend ν_4 PtX_3 bend
A_2 (inactive)	ν_5 C_3PtX_3 twist
E (i.r. and R.)	ν_6 Pt–C stretch ν_7 Pt–X stretch ν_8 PtC_3 bend ν_9 PtX_3 bend ν_{10} C_3PtX_3 rock

Pt–C Stretching (A_1 + E) and Internal Methyl Modes

The Pt–C stretching vibrations give in general very weak infrared bands and often cannot be assigned with any confidence. In the Raman spectra they are quite intense. For $(CH_3)_3PtCl_3^{2-}$, only one band at 585 cm^{-1} was observed, which is a superimposition of A_1 and E vibrations. The same was found for powder spectra of $(CH_3)_3PtBr_3^{2-}$ (569 cm^{-1}), while the solution spectrum exhibits two bands at 573 and 565 cm^{-1}. Polarization measurements show that one of these is polarized and can be assigned to a vibration of A_1 species. Under the resolution of the experiment, this cannot unequivocally be recognized as the higher frequency band; however, in the Raman spectra of the trimethylplatinum(IV) chloride and iodide tetramers[11] where $\Gamma_{Pt-C} = A_1 + E + 2T_2$, the bands at 583 and 568 cm^{-1} (higher frequencies) are the ones of A_1 species. The Pt–C stretching frequencies appear to follow the same trend with the "trans" ligand as found for the parent halides: $(CH_3)_3PtX_3^{2-}$ = 585, 569 cm^{-1}; $X = Cl^-, Br^-$; $[(CH_3)_3PtX]_4$ = 581, 574, 564 cm^{-1} (average of Raman active vibrations), $X = Cl^-, Br^-, I^-$.[11,12] In the 1200–1300 cm^{-1} region (see Table IV) only one band is observed in the Raman and two in the infrared. They are assigned to symmetric deformations of the methyl groups. The asymmetric methyl deformation frequency, which appears as a weak, broad band at about 1415 cm^{-1} in the neutral halides,[12] could not be identified, while a medium intensity band at ca. 2810 cm^{-1} (infrared) is tentatively assigned to the overtone of the asymmetric methyl deformation. The number of experimental frequencies is therefore much less than the five frequencies ($2A_1 + 3E$, as A_2 is inactive) which are expected to be active both in the Raman and the infrared.

Pt–X stretching frequencies

The Pt–X coordinates transform according to the same representation as for the Pt–C coordinates ($A_1 + E$). The Pt–X stretching vibrations could be observed only in the infrared spectrum. The $(CH_3)_3PtCl_3^{2-}$ spectrum shows a weak, broad band at 282 cm^{-1}, (288 cm^{-1} for the complex bromide) which is tentatively assigned to a PtC_3 deformation mode. The medium intensity band at 212 cm^{-1} should therefore be associated with a Pt–Cl stretching vibration (216 cm^{-1} in the neutral halide). Analogously, the group of frequencies observed at 172, 151 and 136 cm^{-1} is tentatively associated with Pt–Br stretching vibrations. The calculated ratio of the stretching frequencies ν_{av}(Pt–Br)/(Pt–Cl) is 0.72. This supports the assignments, since this ratio is usually ca. 0.70 for complex anions.[18] The similarity of the terminal Pt–X stretching frequencies of $(CH_3)_3PtX_3^{2-}$ with the Pt–X bridge stretching frequencies[11,12] is unexpected, as it seems very likely that Pt–Cl stretching force constants will be lower for the bridges. However, for $[(CH_3)_2AuCl]_2$ (273 cm^{-1})[7] and $(CH_3)_2AuCl_2^-$ (281 cm^{-1})[19] no remarkable difference was found for similar frequencies. As expected, a sharp decrease in frequency is noticed in Pt–X stretching frequencies relatively to those of PtX_6^{2-} ions.[20] This drop in frequency caused by the replacement of three halide ions of PtX_6^{2-} with three "methide" ions focuses the attention on the "trans" influence of methyl groups in organometallic moieties. A similar effect was found in going from $AuCl_4^-$ to $(CH_3)_2AuCl_2^-$.[19] For trimethylplatinum(IV) and dimethylgold(III) derivatives, it seems that the "trans" bond weakening effect of the methyl ligands is very similar in both the neutral polynuclear molecules and anionic complexes.

ACKNOWLEDGEMENTS

The financial support by C.N.R. (Roma) is acknowledged.

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