Metal–Olefin Complexes. Part II.[1] Some Palladium(II) and Platinum(II) Derivatives of Tris(but-3-enyl)arsine containing Co-ordinated and Unco-ordinated Olefinic Groups

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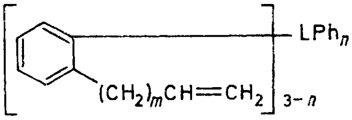
The potentially quadridentate chelate, tris(but-3-enyl)arsine, reacts with palladium(II) salts to form $PdLX_2$ (X = Cl, I) complexes, and with platinum(II) salts to form $PtLX_2$ (X = Cl, Br, I, CNS) complexes. The complexes have been investigated by conductivity measurements, molecular weight studies, and by electronic, i.r., and ^1H n.m.r. spectroscopy. The $PdLCl_2$ and $PtLX_2$ (X = Cl, Br) complexes are *cis*-planar and, as well as containing an arsine donor, also contain a co-ordinated olefinic group in rapid equilibrium with unco-ordinated olefins. The $PdLI_2$ and $PtLX_2$ (X = I, CNS) are halogeno- or pseudohalogeno-bridged dimers and contain only monodentate arsine-donor ligands. The tendency for olefins to co-ordinate in these, and analogous systems, is discussed.

SEVERAL transition metal complexes containing chelating ligands with one phosphorus or arsenic donor atom and olefinic groups have been characterised. These ligands

$Ph_nL[(CH_2)_mCH{=}CH_2]_{3-n}$ $n = 1, 2,\ m = 3,\ L = P, As$

$n = 0,\ m = 2,\ L = P$

(i)



$n = 0, 1, 2,\ m = 0, 1$

$L = P, As$

(ii)

have been of two main types, (i) and (ii), with (ii) being the more sterically rigid.[1-3] The co-ordination chemistry of such ligands with d^8 ions, notably Rh^I, Ir^I, Pd^{II}, and Pt^{II}, has been extensively studied.[2] Recently Clark and Hartwell[4] characterised a five-co-ordinate rhodium(I) complex with tris(but-3-enyl)phosphine. Structural investigations suggested a monomeric trigonal bipyramidal co-ordination about the rhodium atom with all four donor sites co-ordinated.

We wish to report here the synthesis of the tertiary arsine tris(but-3-enyl)arsine, and some palladium(II) and platinum(II) complexes with this ligand. The co-ordination chemistry of this ligand has proved to be of interest because, in its reaction with Rh^I salts, its behaviour is different from that of the analogous phosphine.[5] This ligand is the first in a series of mixed arsine-olefin multidentates of the general formula $(CH_2{=}CHCH_2CH_2)_nAs(CH_2CH_2CH_2AsMe_2)_{3-n}$ which we have synthesised.

EXPERIMENTAL

Physical measurements were obtained as previously described.[6]

Synthesis of 4-*Chlorobut*-1-*ene*.—4-Chlorobut-1-ene was prepared by the method of Roberts and Mazar[7] with one modification. Tetrahydrofuran (THF) was found to be a more efficient solvent for the Grignard reaction. The product was obtained as a colourless liquid, b.p. 74° at 750 mmHg (literature 72—74°) (yield 45%).

Synthesis of Tris(*but*-3-*enyl*)*arsine*.—A Grignard reagent was prepared from 4-chlorobut-1-ene (25 g, 0·273 mol), dry THF (60 ml), and magnesium (7·2 g, 0·296 mol) in dry THF (250 ml) and arsenic trichloride (15 g, 0·085 mol) in THF (150 ml) was added to it at −10 °C. The mixture was then refluxed for 30 min and the excess of Grignard reagent destroyed by careful addition of aqueous ammonium chloride (35 g in 300 ml water) at 0 °C. The upper organic layer was separated, dried (sodium sulphate), and the volatile materials removed under reduced pressure. The arsine was obtained as a colourless oil, b.p. 101° (3 mmHg) (yield of the air-sensitive product 20 g, 60%).

A derivative was prepared as follows. Tris(but-3-enyl)arsine (1·0 g, 4·17 mmol) in anhydrous ether (5 ml) was added dropwise to an excess of methyl iodide (4·0 g) in refluxing ether (25 ml). The white precipitate was collected on a sinter and recrystallised from ether–ethanol to yield colourless crystals, 1·05 g (66%) (Found: C, 41·1; H, 6·4; I, 33·1. $C_{13}H_{24}AsI$ requires C, 40·9; H, 6·3; I, 33·2%).

Preparation of $PtCl_2As(CH_2CH_2CH{=}CH_2)_3$.—Tris(but-3-enyl)arsine (0·56 g, 2·06 mmol) in ethanol (5 ml) was added dropwise over a period of 5 min to a gently refluxing solution of dipotassium tetrachloroplatinate(II) (1·0 g, 2·06 mmol) in ethanol (15 ml). The solution gradually became pale yellow (30 min). The solution was evaporated to dryness, leached with dichloromethane, and filtered. Careful addition of di-isopropyl ether followed by cooling gave colourless crystals, which were recrystallised from isopropyl alcohol to yield 0·6 g (72%). Complexes of the type $PtX_2As(CH_2CH_2CH{=}CH_2)_3$ were prepared similarly in the presence of a molar excess of the appropriate sodium salt.

Preparation of $PdCl_2As(CH_2CH_2CH{=}CH_2)_3$.—Tris(but-3-enyl)arsine (0·75 g, 2·38 mmol) in ethanol (5 ml) was added over 5 min to disodium tetrachloropalladate(II) (0·7 g, 2·38 mmol) in ethanol (15 ml) under nitrogen. The solution rapidly turned yellow, and was refluxed for a further 30 min. The solution was evaporated to dryness, leached with dichloromethane, and the sodium halide filtered off. Careful addition of isopropyl alcohol, and concentration of the solution precipitated yellow crystals (yield 0·95 g, 95%).

Preparation of $PdI_2As(CH_2CH_2CH{=}CH_2)_3$.—Sodium iodide (0·75 g, 5·0 mmol) was added to disodium tetrachloropalladate(II) (0·25 g, 0·85 mmol) in refluxing ethanol (15 ml)

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[1] Part I, I. Baillie, B. L. Booth, and C. A. McAuliffe, *J. Organometallic Chem.*, 1973, **59**, 247.

[2] F. R. Hartley, *Chem. Rev.*, 1969, **69**, 799.

[3] H. W. Kouwenhoven, J. Lewis, and R. S. Nyholm, *Proc. Chem. Soc.*, 1961, 220; R. S. Nyholm, *Pure Appl. Chem.*, 1970, **27**, 127.

[4] P. W. Clark and G. E. Hartwell, *Inorg. Chem.*, 1970, **9**, 1948.

[5] C. A. McAuliffe and D. G. Watson, unpublished results.

[6] L. Baracco and C. A. McAuliffe, *J.C.S. Dalton*, 1972, 948.

[7] J. O. Roberts and R. H. Mazar, *J. Amer. Chem. Soc.*, 1951, **73**, 2509.

under nitrogen. Tris(but-3-enyl)arsine (0·20 g, 08·3 mmol) in ethanol (5 ml) was added over 5 min. The solution rapidly turned deep red, and the solution was refluxed for a further 30 min. The mixture was evaporated to dryness, leached with chloroform, and filtered. Careful addition of di-isopropyl ether to the dark red filtrate precipitated dark red, almost black crystals (yield 0·40 g, 80%).

Attempted Preparation of $PdX_2As(CH_2CH_2CH{=}CH_2)_3$ ($X = Br$ *and* CNS).—Attempts to prepare these complexes, both by the appropriate metathetic reaction or by the addition of the appropriate sodium halide to the chloro-complex, proved unsuccessful. The reaction with sodium thiocyanate yielded intractable yellow oils. The bromo-complex could not be isolated pure, although a small amount of a pale yellow solid was obtained after prolonged work-up.

Attempted preparations of nickel and cobalt analogues were not successful.

RESULTS AND DISCUSSION

Palladium Complexes.—The complexing ability of tris(but-3-enyl)arsine was investigated with several d^8 metal ions. That no complex appeared to form with $NiCl_2$ or $CoBr_2$, even in the presence of a ten-fold excess of neat ligand, is in accord with the well known low affinity of these metal ions towards monodentate arsines.[8]

TABLE 1

Analytical data and some physical properties of the complexes

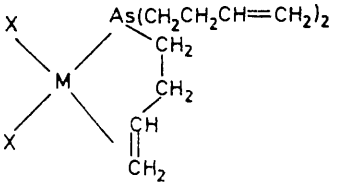
Complex [a]	Colour	M.p. [b] (t/°C)	% Calc. C	H	Hal	% Found C	H	Hal	M [c]
$PdLCl_2$	Yellow	105	34·5	5·1	17·0	34·5	5·0	16·9	441 (418)
$PdLI_2$	Dark red	142	24·1	3·5	42·4	24·5	3·8	42·2	*d*
$PtLCl_2$	Colourless	122	28·5	4·2	14·0	28·5	4·2	13·9	464 (506)
$PtLBr_2$	Colourless	135	24·2	3·6	26·9	24·2	3·8	26·8	576 (595)
$PtLI_2$	Red-brown	139	20·9	3·1	36·8	23·3	3·3	36·5	*d*
$PtL(CNS)_2$	Yellow	140 dec.	31·1	3·8		30·8	3·4		*d*

[a] All complexes are non-conductors in nitromethane and dichloromethane. [b] Uncorrected. [c] In dichloromethane solution, calc. (found). [d] Too insoluble for measurement.

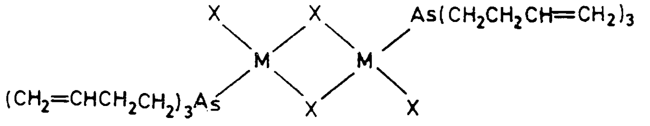
The chloro-complex, $PdLCl_2$, is monomeric in dichloromethane (Table 1), and is non-conducting in dichloromethane and nitromethane. The iodo-complex is insufficiently soluble in any suitable solvent for meaningful physical data to be obtained in the solution state.

The solid state and solution electronic spectra of the chloro-complex exhibit no absorptions below 28 10^3cm^{-1}. There is an intense absorption band at 41·8 10^3cm^{-1} and shoulders at 37 and 28·2 10^3cm^{-1}. The solid state spectrum of the iodo-complex is ill defined, but no absorption bands are present below 28 10^3cm^{-1}. The presence of a band in the 20—25 10^3cm^{-1} region is diagnostic of a five-co-ordinate palladium(II) chromophore,[9] and thus it may be concluded that the electronic spectral data suggest that these complexes are not five-co-ordinate, but are probably square planar.

On the basis of these analytical data, conductance, and spectral measurements, (I) and (II) represent possible structures.



(I)



(II)

The Nujol mull i.r. spectra of the two complexes (Table 2) exhibit a sharp band of medium intensity at 1635 cm^{-1} (ligand 1675). Many workers have assigned similar bands to ν(C=C), although Hiraishi [10] has assigned this band to mixing of ν(C=C) and a C–H deformation on the basis of co-ordinate analysis and deuteriation studies. A weaker band at 1522 cm^{-1} present in the spectrum of the chloro-complex, but absent from that of the iodo-complex, is in the region (*ca.* 1530 cm^{-1}) thought to indicate the presence of a palladium–olefin bond.[11] The chloro-complex shows a medium band at 425 cm^{-1} which is assigned to ν($Pd{-}C_2$) in accord with a similar assignment of a band at 427 cm^{-1} in $[Pd_2Cl_4(C_2H_4)_2]$.[12] Grogan and Nakamoto have suggested the use of metal–olefin stretching frequency as diagnostic of both metal–olefin bond formation and strength.[13] Strong absorption bands at 315 and 268 cm^{-1} in the chloro-complex are assigned to ν(Pd–Cl), consistent with a *cis* structure. A *trans* isomer would have only one metal–halogen stretch, while a dimeric structure would have three bands.[14] Both complexes exhibit a band of medium strength at 290 cm^{-1}, which

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[8] J. C. Cloyd, jun., and C. A. McAuliffe in ' Aspects of Inorganic Chemistry,' vol. 1, Macmillan, London, 1973.

[9] G. Dyer and L. M. Venanzi, *J. Chem. Soc.*, 1965, 2771.

[10] J. Hiraishi, *Spectrochim. Acta*, 1969, **25A**, 749; J. Hiraishi, D. Friseth, and F. A. Miller, *ibid.*, p. 1657.

[11] D. B. Powell and N. Sheppard, *Spectrochim. Acta*, 1958, **13**, 69.

[12] M. J. Grogan and K. Nakamoto, *J. Amer. Chem. Soc.*, 1966, **88**, 5454.

[13] M. J. Grogan and K. Nakamoto, *J. Amer. Chem. Soc.*, 1968, **90**, 918.

[14] R. J Goodfellow, P. L. Goggin, and L. M. Venanzi, *J. Chem. Soc. (A)*, 1967, 1897.

is assigned to ν(Pd–As).[14,15] The spectrum of the iodo-complex is much simpler (Table 2), and shows no indications of metal–olefin bonding. On the basis of this evidence, the chloro-complex is assigned structure (I), and the iodo-complex structure (II).

The solution i.r. spectrum of the chloro-complex is much simplified, and differs from that of the ligand and the solid complex in several areas (see Table 2). Interestingly, a strong band appears at 1640 cm^{-1}, but there is no band in the 1530 cm^{-1} region. Nyholm has postulated[16] that in complexes where one, but not all, olefin groups are co-ordinated, there exists a rapid bonded $\rightleftharpoons$ non-bonded equilibrium, which is slow enough in the solid state, if it occurs at all, to allow identification of both types by i.r. spectrum. In solution this type of equilibrium must be so rapid that an averaged spectrum is seen.

TABLE 2

Some significant infrared absorptions/cm^{-1}

	Free ligand	$PdLCl_2$	$PdLCl_2$ [a]	$PdLI_2$	$PtLCl_2$	$PtLBr_2$	$PtLI_2$	$Pt(CNS)_2$
ν(=CH_2)	3075s	3075, 3062ms 3055sh		3070m	3070m 3060s	3035, 3030ms	3070w	3075m
ν(CN)								2110s 2065s
‘ ν(C=C) + δ(C–H) ’ (free)	1675vs	1633ms	1640s	1635m	1635m	1635m	1635m	1632m
‘ ν(C=C) + δ(C–H) ’ (co-ord.)		1522m			1493m	1495m		
ν(As–C)	580mw 552mw	585sh 542m		585w 553w				
ν(Pt–C_2)$_{asym}$	440mw				470, 440w	470, 440w		
ν(M–Hal)	315vs				330vs 295w			
ν(M–As)	290ms 286vs [b]			295m	280s	310w		

[a] In dichloromethane; other spectra in Nujol. [b] (Pd–Cl).

The n.m.r. spectrum of the chloro-complex is consistent with the type of equilibrium outlined above, and is discussed below.

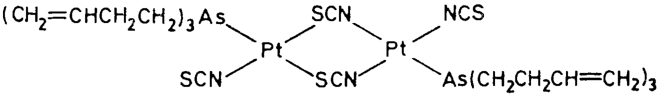
Platinum Complexes.—All four complexes are non-conductors in nitromethane and dichloromethane, measurements on the iodo- and thiocyanato-complexes being taken on the solutions before isolation. Molecular weight determinations in dichloromethane indicate the chloro- and bromo-complexes are monomeric.

The absence of an absorption band in the reflectance spectra of the bromo- and iodo-complexes in the 20 to 25 10^{3}cm^{-1} region precludes a five-co-ordinate structure. In solution, the bromo-complex shows a strong assymetric peak around 42 10^{3}cm^{-1}, with a weaker peak at 35·7 10^{3}cm^{-1}, consistent with a square planar structure.

I.r. spectra of the iodo- and thiocyanato-complexes are preponderantly alike in solid and CH_2Cl_2 solution, and resemble the $PdLI_2$ complex (Table 2). In the spectra of the chloro- and bromo-complexes in Nujol, as well as the band at 1635 cm^{-1}, a new band appears *ca.* 1495 cm^{-1}, in good agreement with assignments in other platinum–olefin complexes.[2,11] Medium bands at 470 and 395 cm^{-1} are assigned to the assymmetric and symmetric ν(Pt–C_2) stretches respectively.[13] Strong absorption bands at 330 and 295 cm^{-1} in the chloro-complex are assigned to ν(Pt–Cl) vibrations, indicating a *cis*-square planar structure (*cf.* 312 and 294 cm^{-1} in $PtLCl_2$, where L = *o*-styryldimethylarsine[17]). Solution spectra of the chloro- and bromo-complexes are very similar to that of $PdLCl_2$ and are much simplified: the band *ca.* 1500 cm^{-1} disappears, both complexes showing a strong sharp band at 1640 cm^{-1}.

It can thus be concluded that the chloro- and bromo-complexes are of structure (I), while the iodo-complex has structure (II).

The solid i.r. spectrum of the thiocyanato-complex shows, by similar reasoning, that the ligand is acting as a monodentate arsine. The i.r. spectrum in the 2100 cm^{-1} region consists of two strong bands at 2110 and 2065 cm^{-1}, assignable to bridging –NCS– and terminal –NCS groups, respectively.[18] A weak band at 850 cm^{-1}, absent from the spectra of the halogeno-complexes, is assigned to ν(CS), again in accord with *N*-bonding.[19] Thus structure (III) is indicated. Unfortunately extreme insolubility in appropriate solvents prevented solution studies, although solution spectra of the complex prior to isolation are broadly similar to the solid spectra.



(III)

N.M.R. Results.—The ^1H n.m.r. spectrum of the ligand tris(but-3-enyl)arsine (Table 3) consists of four main groups of absorption: a multiplet of ten peaks, centred τ *ca.* 4·25; a close doublet at τ 5·0 and a complex doublet at τ 5·1; a complex quartet at τ 7·85 and a complex triplet at τ 8·6. The profile is very similar to

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[15] R. J. Goodfellow, J. G. Evans, P. L. Goggin, and D. A. Duddell, *J. Chem. Soc.* (*A*), 1968, 1604.

[16] D. I. Hall and R. S. Nyholm, *J. Chem. Soc.* (*A*), 1971, 1491.

[17] M. A. Bennett, J. Chatt, G. J. Erskine, J. Lewis, R. F. Long, and R. S. Nyholm, *J. Chem. Soc.*, 1967, 501.

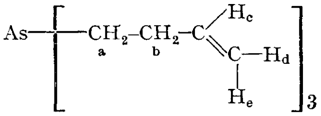
[18] J. L. Burmeister, *Co-ordination Chem. Rev.*, 1966, **1**, 205, and references therein.

[19] R. A. Bailey, S. L. Kozak, T. W. Michelsen, and W. N. Mills, *Co-ordination Chem. Rev.*, 1971, **6**, 407.

the spectrum reported for the analogous phosphine,[4] and has been assigned correspondingly (Table 3).

TABLE 3

N.m.r. results



Chemical shift [a]

Proton	Free ligand	$PtBr_2L$	$PdCl_2L$
H_a	8·6 (t)	8·4 (vw)	8·34 (vw)
H_b	7·9 (q)	7·89 (t)	7·5 (t)
H_c	4·25 (m)	4·45 (m)	3·99 (m)
H_d	5·13 (d)	5·28 (d)	5·13
H_e	5·0	5·05 (t)	4·86 (t)

Coupling constants

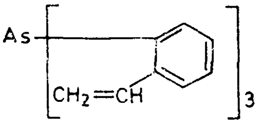
	Free ligand	$PtBr_2L$	$PdCl_2L$
J_{cd}	9·0	10·0	10·0
J_{ce}	18·0	15·0	16·0

[a] Relative to tetramethylsilane, τ 10·0 p.p.m.

In the case of a metal complex where some of the olefin groups are unco-ordinated, it might be expected that the n.m.r. spectrum would consist of absorptions characteristic of free and co-ordinated olefin groups. This type of spectrum is not found in practice for reasons of the rapid equilibria discussed before. Solutions ($CDCl_3$) of considerable concentration were needed for good spectra, and solubility problems restricted studies to $PdLCl_2$ and $PtLX_2$ (X = Cl, Br).

A tentative assignment is given in Table 3; previous workers [16] have observed such types of profile, and our results are in agreement with the concept of rapid bonded–non-bonded equilibria in solution.

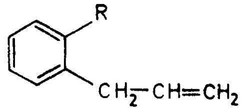
The platinum bromide complex with the potentially quadridentate ligand (IV) gives a simplified n.m.r. spectrum in $CDCl_3$, consisting of four absorptions in the intensity ratios of 4 : 1 : 1 : 1. The change in chemical shift on going from free ligand to complexed ligand were found to be less than 1 p.p.m.[16]



(IV)

CONCLUSION

Previous results have shown that the substitution of an apical arsenic atom for phosphorus in chelating olefins can have important effects on the co-ordinating properties of the ligand. On the basis of experimental results with the ligands AP and AA, the former was considered to be the better chelate, *e.g.* the complex $Pt(AP)(CNS)_2$ contains metal olefin bonding, while the arsine analogue has the empirical formula $Pt(AA)_2(CNS)_2$ with no metal–olefin bonding.[17] Although the ligand $P(CH_2CH_2CH{=}CH_2)_3$ has been studied,[4] its platinum and palladium complexes have not been reported. Thus a direct comparison could not be made. Comparisons with the ligands $R_2P(CH_2CH_2CH{=}CH_2)$ (where R = cyclohexyl and ethyl) are similarly uninstructive; the



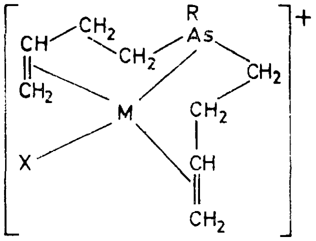
(AA) R = $AsMe_2$
(AP) R = PPh_2

only complexes reported are the $MLCl_2$ (M = Pt, Pd) species, in both of which the ligand acts as bidentate.[20]

The concept that the platinum–olefin bonding is stronger than the palladium–olefin bonding in comparable compounds has received general acceptance; [13] thus platinum–olefin complexes are more easily isolated than their palladium analogues. We find that while the chloro-complexes of both metals contain metal–olefin bonding, the only chelated bromo-complex is that of platinum.

For both metals, the tendency to form chelated complexes is effected by the anion present. Iodide and especially thiocyanate ion tend to displace the co-ordinated double bond.[21] Our results are in agreement with this conclusion; the series of platinum complexes gives the normal order Cl $\sim$ Br $<$ I $\ll$ CNS.

Even in the case of platinum, a chelated arsine-olefin complex with thiocyanate ion has not been reported,[2] reactions of metal–olefin halides with an excess of sodium thiocyanate usually resulting in monomolecular species of the type $ML_2(CNS)_2$. It is perhaps surprising that we were unable to isolate a similar complex, even with a five-fold excess of thiocyanate ion. Presumably, the bulky nature of the butenyl groups, and their flexibility, provide steric hindrance against the formation of a bis complex.



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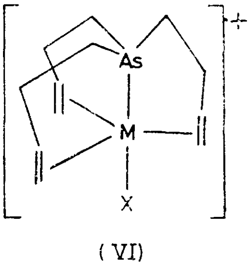

(VI)

Initial studies on ligands with a flexible pentenyl

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[20] K. Issleib and M. Haftendorn, *Z. anorg. Chem.*, 1967, **351**, 9.

[21] I. Leden and J. Chatt, *J. Chem. Soc.*, 1955, 2936.

group[22] showed that such ligands chelated to Pt but not to Pd. Steric restrictions were considered insufficiently stringent to make these pentenyl ligands good chelate groups for any transition metal other than platinum. However, it has already been noted that palladium complexes of (but-3-enyl)diethylphosphine with co-ordinated olefin were isolated when the anion was chloride.[20] The preparation of a chelated $PdCl_2$ complex with tris(but-3-enyl)arsine, containing a similar olefin backbone, suggests that the steric factors and chelate chain length are important and subtle in effect.

The failure to isolate a five-co-ordinate complex is not surprising in the light of the flexibility of the ligand. Even for the more sterically constrained ligand (IV), five-co-ordinate species could not be isolated.[16] Several attempts to force five-co-ordination upon the metal ions by the addition of non-complexing ions (perchlorate and tetraphenylborate) result in the rapid decomposition of the complexes (both platinum and palladium) and the deposition of the metal. This is presumably due to the contraction of the bonding *d* orbitals of the metal atom upon forming a cationic complex of the type (V) and (VI).

[3/1655 *Received, 6th August,* 1973]

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[22] M. A. Bennett, H. W. Kouwenhoven, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1964, 4570.