

PLATINUM(II) COMPLEXES INCORPORATING THE
CHELATING DIARYL DITELLURIDE LIGANDS
{ArTe-TeAr} (Ar = Ph, PhOCH₃, PhOC₂H₅, PhOPh)
AND APPLICATIONS TO CATALYSIS

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ABSTRACT

Platinum(II) complexes of the type [Pt{ArTe-TeAr}Cl₂] (Ar = C₆H₅, C₆H₄OCH₃, C₆H₄OC₂H₅, C₆H₄OC₆H₅) 5, 6, 7 and 8 respectively have been made via transmetallation reaction with the diarylditelluride {ArTe-TeAr} (Ar = C₆H₅, C₆H₄OCH₃, C₆H₄OC₂H₅, C₆H₄OC₆H₅) 1, 2, 3 and 4 respectively and K₂[PtCl₄].

Attempts to activate platinum (II) dichloro complexes incorporating {ArTe-TeAr} (Ar = C₆H₅, C₆H₄OCH₃, C₆H₄OC₂H₅, C₆H₄OC₆H₅) 5, 6, 7 and 8 respectively, with dimethyl as ligands were unsuccessful.

INTRODUCTION

Over 40 years have past since the discovery by Karl Ziegler that ethylene could be polymerised under extremely mild conditions by transition metal catalysis.

The early transition metals have been predominantly the basis of the catalysts [Hagen et al., (2002)].

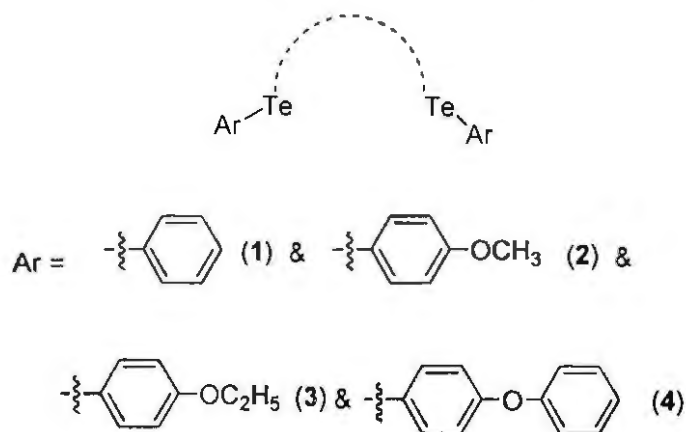
Platinum organometallic compounds incorporating telluride and selenid type ligands are widespread throughout the literature, and they are still unknown for application in catalysis. Previously reports have described some diorganotelluride complexes with palladium(II) and platinum(II) for example, {[(PhCH₂)₂Te]₂PtCl₂} was reported by [Fritzman & Anorg (1924)].

More relevant to the present investigation is Jensen's claim that the reaction of K_2PtCl_4 with diphenyl telluride in ethanol affords $cis\text{-}\{Pt(Ph_2Te)_2Cl_2\}$ [Jensen & Anorg (1937)].

Chatt and co-workers synthesised some dialkyl telluride complexes of palladium(II) and platinum(II). The $trans\text{-bis}(\text{dialkyl telluride})$ complexes, $\{(R_2Te)_2PdX_2\}$ reacted with Grignard reagents afford $\{(R_2Te)_2Pd(R')\}$ ($R' = Ph, O\text{-tol}, O\text{-ClC}_6\text{H}_4, p\text{-ClC}_6\text{H}_4$; Comparing these results with other work with dialkyl sulphide and $X = \text{halogen}$) selenide complexes afforded a trend in the stability of $\{Pd(Et_2M)(R)X\}$ of ($M = S < M = Se < M = Te$) [Sergi et al., (1970)]. The view was again expressed that π -bonding was more important in the selenium and tellurium cases. [Chatt et al., (1955)].

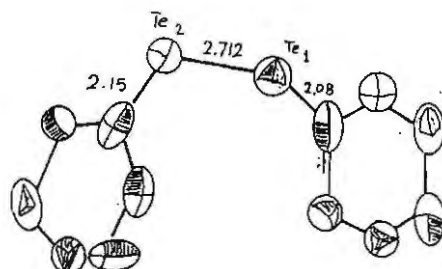
The kinetic factors as by any tendency of tellurium to accept d electrons from platinum were studied by Chia and his group using far infrared spectra of $\{Pd(Ph_2Te)_2X_2\}$. The Oxidative addition of two diorganoditellurides to $\{Pd(PPh_3)_4\}$ was demonstrated by the same group. [Chia & McWhinnie (1978)].

The chelating diaryl ditelluride are applied to the coordination chemistry of platinum(II). In this paper, one of our goals was to treat a variety of bulky, chelating diaryl ditelluride ligands with $K_2 [PtCl_4]$ and study the steric effects of the diaryl ditelluride ligands incorporating the voluminous $C_6H_5, C_6H_4OCH_3, C_6H_4OC_2H_5, C_6H_4OC_6H_5$ groups (Scheme 1).



Scheme 1

These kind of ligands are extremely light sensitive and will decomposed in light [Mehdi et al., (1984)]. Diaryl ditelluride (1- 4) were prepared as in literature, [Mehdi & Miller (1984)]. and X-ray of diphenyl ditelluride was showed in fig. 1 [Allkins & Hendra (1967)].

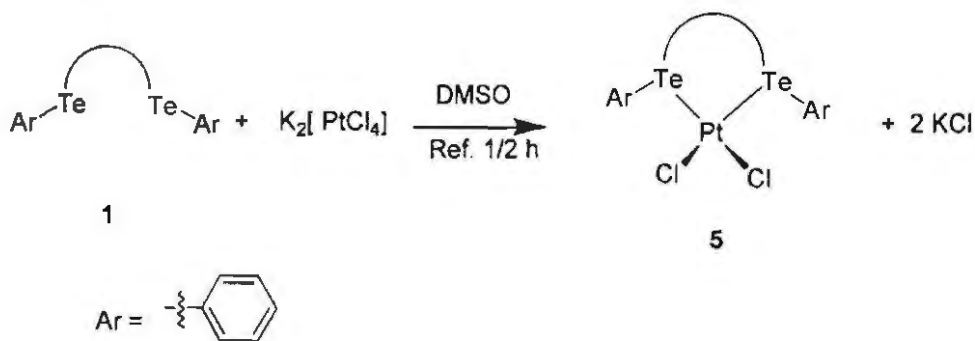


Experimental and results:-

Palladium(II) diphenyl ditelluride complex:-

Potassium tetrachloropalladium(II) was reacted with one equivalent of diarylditelluride 1 in DMSO at room temperature which resulted in a precipitate of insoluble potassium chloride. The mixture was warmed up to 40 °C for 30 minutes with stirring. Work-up yielded [Pt{ArTeTeAr}Cl₂], (5) as a brown, crystalline material in 60% yield after slow cooling of an Et₂O solution to - 40 °C (Scheme 2).

Scheme 2



The ultraviolet (UV) spectrum confirmed the constitution of 5, which shows square symmetry spectrum. The tellurium donors chelate around the platinum centre plus two chloride as co-ligands as expected,

and the metal centre resides in a square geometry environment. The chelates of these ligends around the metal ion, also were identified by infrared (IR) spectrum which showed the $\text{Te}\bar{\text{P}}\text{t}\bar{\text{Te}}$ and $\text{Cl}\bar{\text{P}}\text{t}\bar{\text{Cl}}$ bonds and a two chloride ligands chelated around the metal centre fig. 1 (Table 1).

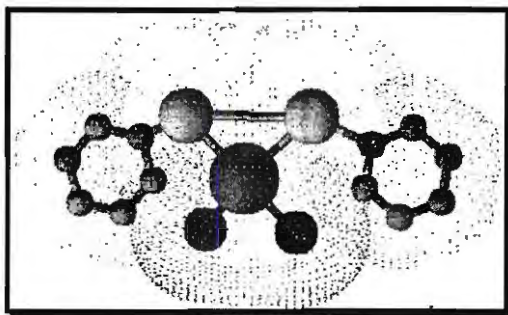
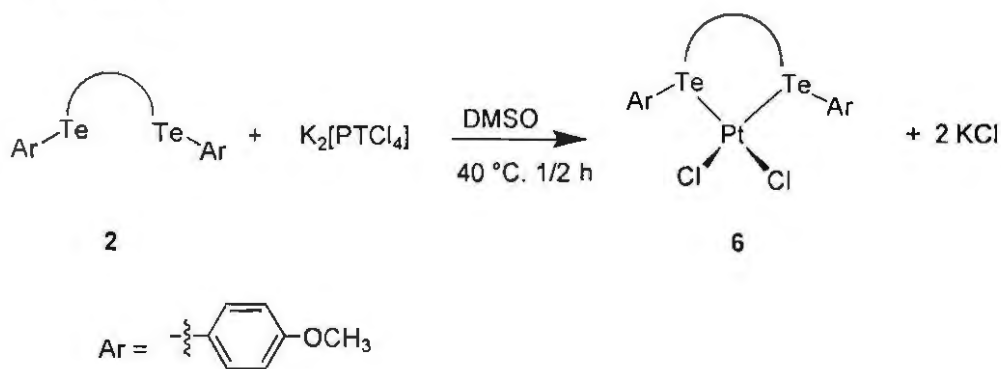


Fig. (2): proposed structure for $[\text{Pt}\{\text{TePh}\}_2\text{Cl}_2]$ (5) (ACD/3D-Viewer)

Again, the reaction between stoichiometric amounts of $\text{K}_2[\text{PtCl}_4]$ and the para-methoxy phenyl **2** in DMSO was performed as for the synthesis of **5**. However, the reaction yielded a brown product. The product identified as the platinum (II) complex $[\text{Pt}\{\text{TeC}_6\text{H}_4\text{OCH}_3\}_2\text{Cl}_2]$ (**6**) (Scheme 3). Brown crystals were obtained from Et_2O at -40°C in 65% yield.

Scheme 3



The complex was characterized by elemental analysis, IR spectra (Table 1) and UV spectra (Table 2).

The geometry of this complex $[Pt\{ArTe\}_2Cl_2]$ ($Ar = C_6H_4OCH_3$) **6** has been studied by UV, which shows square symmetry spectrum fig. 3.

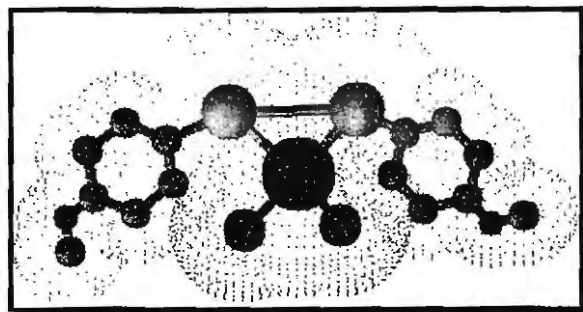


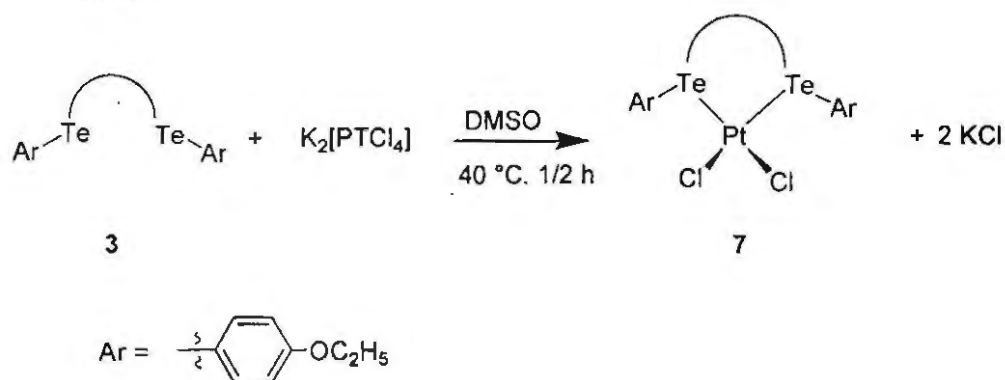
Fig. (3): proposed structure for $[Pt\{Te C_6H_4OCH_3\}_2Cl_2]$ (**6**) (ACD/3D-Viewer)

The para-methoxy phenyl telluride **2** should offer more protect the metal ion than phenyl telluride **1**.

Dichloro bis(p-ethoxy phenyl telluride) platinum(II):-

To a slurry of $K_2[PtCl_4]$ (0.2 g, 0.751 mmol) in DMSO (30 mL), was added a solution of **3** (0.372g, 0.751 mmol) in DMSO (30 mL) at room temperature and then the reaction mixture was warmed up to $40^\circ C$ for $\frac{1}{2}$ hour with stirring. After which time it was filtered. The volume of solvent was removed and the product was dissolved in 20 mL of ether and brown crystals of $[Pt\{ArTe-TeAr\}Cl_2]$ ($Ar = C_6H_5OC_2H_5$) **7** were obtained after 24 h at room temperature (65 %) Scheme 4.

Scheme 4



Spectroscopic measurements; UV and IR spectra were determined for 7. UV spectral data for 8 was given in table 1. IR spectrum data showed in table 2. The conformation from IR and UV is given in Fig. 4.

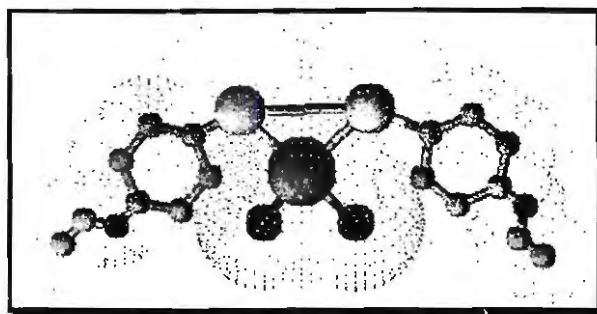


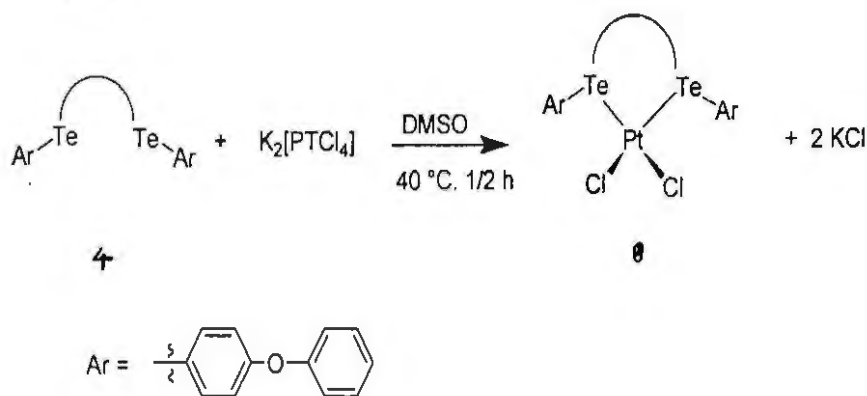
Fig. (4): proposed structure for $[\text{Pt}\{\text{Te C}_6\text{H}_4\text{OC}_2\text{H}_5\}_2\text{Cl}_2]$ (7) (ACD/3D-Viewer)

1 should less vacant space around the metal centre than the 2. Hence, it would be expected that ethylene polymerisation would be most successful when using the *para*-methoxy phenyl ligand.

Dichloro bis(*p*-phenoxy phenyl telluride) platinum(II) (8):-

The reaction between stoichiometric amounts of $\text{K}_2[\text{PtCl}_4]$ and the *para*-phenoxy phenyl telluride 4 in DMSO was performed as for the synthesis of 7. However, the reaction yielded a different product: a brown product, which was identified as the platinum(II) complex $[\text{Pd}\{\text{Te}(\text{C}_6\text{H}_4\text{OC}_6\text{H}_5)\}_2\text{Cl}_2]$ (8) (Scheme 5). Brown crystals were obtained from Et_2O at -40°C in 40% yield.

Scheme 5



Prior to this work no research had been undertaken with respect to the ethene polymerization diaryl ditelluride incorporating C_6H_5 , $\text{C}_6\text{H}_4\text{OCH}_3$, $\text{C}_6\text{H}_4\text{OC}_2\text{H}_5$, $\text{C}_6\text{H}_4\text{OC}_6\text{H}_5$ groups.

Para-phenoxy phenyl telluride, $[(\text{C}_6\text{H}_4\text{OC}_6\text{H}_5)\text{Te}-\text{Te}(\text{C}_6\text{H}_4\text{OC}_6\text{H}_5)]$, therefore research was initiated to examine the effects upon coordination geometry by an extra-long phenoxy ligand. Fig. 5.

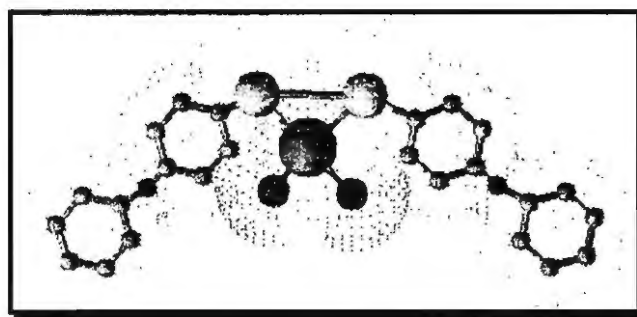


Fig. 5 proposed structure for $[\text{Pt}\{\text{Te C}_6\text{H}_4\text{OC}_6\text{H}_5\}_2\text{Cl}_2]$ (8) (ACD/3D-Viewer)

Far and Infrared spectra dissection of palladium complexes

The solubility of the diaryl ditelluride complexes $[\text{Pt}(\text{TeAr})_2\text{Cl}_2]$ ($\text{Ar} = \text{C}_6\text{H}_5$, $\text{C}_6\text{H}_4\text{OCH}_3$, $\text{C}_6\text{H}_4\text{OC}_2\text{H}_5$, $\text{C}_6\text{H}_4\text{OC}_6\text{H}_5$) in benzene, coupled with the observation of two halogen metal stretching frequencies (Fig. 6). The previously been suggested that the tendency to synthesize *cis* complexes of dialkyl tellurides and platinum (II) could be attributed to

significant back bonding from platinum to tellurium which would be more favoured in the *cis* isomer [Allkins & Hendra (1967)].

The four co-ordination complexes were examined by IR spectrum.

The assignments of (MX) (338 cm^{-1}) seems comparable the spectrum to those given for the stretching of non-bridging palladium/platinum halide system generally were found at 344 cm^{-1} . [Allkins & Hendra (1967) and Hendra & Sadasivan (1965)].



Fig. (6): IR Spectroscopy of $[\text{Pt}\{\text{ArTe-TeAr}\}]$ (Ar = C_6H_5 , $\text{C}_6\text{H}_4\text{OCH}_3$, $\text{C}_6\text{H}_4\text{OC}_2\text{H}_5$, $\text{C}_6\text{H}_4\text{OC}_6\text{H}_5$)

The absorption assignment as $\nu(\text{Te-Ph})$ bond in the complexes at 392 cm^{-1} which is consistent with formulation as monomeric *cis* complexes and also within those known in literature. [Cooper (1971)]. C=C bond aromatic were found at frequencies 1422 , 1652 cm^{-1} and C-H bond of aromatics at frequency 3004 cm^{-1} . The appearance of absorption band at 704 cm^{-1} indicates two substitution in aromatic ring in *p*-position to each other. Also, frequency at 2918 cm^{-1} was indicated for C-H aliphatic.

However, the appearance of absorption band at 189 cm^{-1} , which shows the presence of Te-Te bond, is an indication of keeping this band unbroken in the complexes. All these frequencies were comparable to the corresponding $(\text{TeAr})_2$ in other complexes prepared previously.

The rather more full assignments are given in Table 1 for $[\text{Pt}(\text{TeAr})_2\text{Cl}_2]$ (Ar = C_6H_5 , $\text{C}_6\text{H}_4\text{OCH}_3$, $\text{C}_6\text{H}_4\text{OC}_2\text{H}_5$, $\text{C}_6\text{H}_4\text{OC}_6\text{H}_5$).

Table (1): Selected data for 5, 6, 7, 8

Complex	Yield	Colour	Decomposition Temperature (°C)	Analysis (%)		Molecular weight
				C	H	
[Pt{TePh) ₂ Cl ₂]	60	Brown	131	21.3 21.2	1.4 2.5	618.506
[Pt{TePhOCH ₃) ₂ Cl ₂]	65	Brown	124	25 24.2	2.4 3	678.506
[Pt{TePhOC ₂ H ₅) ₂ Cl ₂]	65	Brown	133	706.506
[Pt{TePhOPh) ₂ Cl ₂]	40	Brown	130	708.506

Ultraviolet spectra dissection of palladium complexes:-

Visible-light irradiation of the complexes [Pt(TeAr)₂Cl₂] (Ar = C₆H₅, C₆H₄OCH₃, C₆H₄OC₂H₅, C₆H₄OC₆H₅) in DMSO solution dissociates one molecule of the ligand L as observed UV-vis and IR spectra.

A study of the complexes [Pd{TeAr)₂Cl₂] by UV spectroscopy showed the presence of electronic spectra having maximum absorption at 322 and 372 nm, which in other terms at the frequencies 31055 and 26881 cm⁻¹, respectively.

These frequencies especially for square planer complexes were found similar to that platinum complex that prepared by [Wernberg (1986)].

The absorption of square planar complexes are explained by the electronic transfer within the d orbital as shown below (Fig. 7).

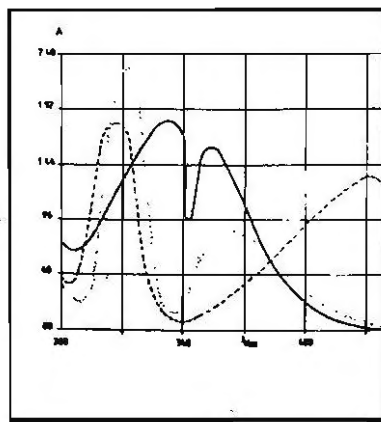
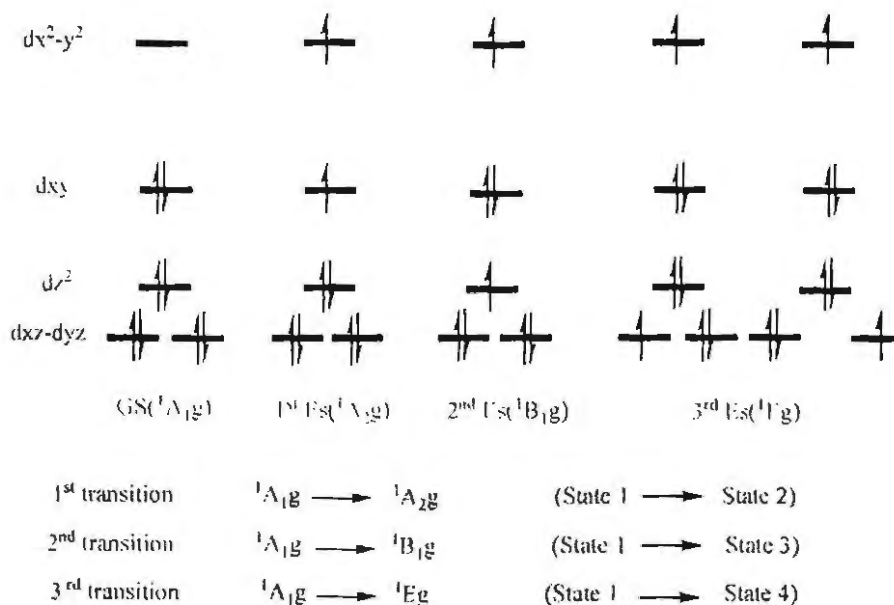


Fig. (7): UV Spectroscopy of (K₂[PtCl₄]), (ArTe-TeAr — — —), ([Pt{ArTe-TeAr}] — — —).

UV-spectra showed the first absorption is due to ${}^1A_{1g} \rightarrow {}^1E_g$ transfer, while the second one is due to ${}^1A_{1g} \rightarrow {}^1A_{2g}$ shift (see scheme 6) and the details are presence in table 2.

Scheme 6



Electronic transition for square planar symmetry

Table (2): Selected UV absorption spectrum of $[Pt(TeAr)_2Cl_2]$ (Ar = C_6H_5 , $C_6H_4OCH_3$, $C_6H_4OC_2H_5$, $C_6H_4OC_6H_5$)

Complexes	λ - Max (nm)	λ - Max (cm^{-1})	d-d traistion
$[Pt(TePh)_2Cl_2]$	322 and 372	31055 and 26881	${}^1A_{1g} \rightarrow {}^1E_g$ and ${}^1A_{1g} \rightarrow {}^1A_{2g}$
$[Pt\{TePhOCH_3\}_2Cl_2]$	330 and 380	30303 and 2615	${}^1A_{1g} \rightarrow {}^1E_g$ and ${}^1A_{1g} \rightarrow {}^1A_{2g}$
$[Pt\{TePhOC_2H_5\}_2Cl_2]$	325 and 375	30769 and 26666	${}^1A_{1g} \rightarrow {}^1E_g$ and ${}^1A_{1g} \rightarrow {}^1A_{2g}$
$[Pt\{TePhOPh\}_2Cl_2]$	328 and 377	30487 and 26525	${}^1A_{1g} \rightarrow {}^1E_g$ and ${}^1A_{1g} \rightarrow {}^1A_{2g}$

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المخلص العربي

متراكبات البلاتين (II) بادخال داياريل دايتيليريد واستخداماته في الحفز

تم تحضير متراكبات البلاتين (II) بادخال داياريل دايتيليريد المختلفه وذلك من خلال تفاعل ترانس يتيال وذلك في محاوله لتنشيط البلاتين ليمنح تطبيقه في مجال الحفز.