# Reactivity of Tetramethylplatinum(IV) Complexes: Thermal Reactions with Electrophiles and Unsaturated Reagents

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## Abstract

The complexes $[PtMe_4(\widehat{N\,N})]$, $\widehat{N\,N}$ = 2,2′-bipyridyl or 1,10-phenanthroline, react with HX to give *fac*-$[PtMe_3X(\widehat{N\,N})]$, where X = Cl, $O_2CCF_3$, $O_2CCH_3$, OPh, SPh, OMe, with $HgCl_2$ to give *fac*-$[PtMe_3Cl(\widehat{N\,N})]$, with $SO_2$ to give *fac*-$[PtMe_3(SO_2Me)(\widehat{N\,N})]$, with $C_2F_4$ to give $[\{PtMe_3(\widehat{N\,N})\}_2(\mu\text{-}C_2F_4)]$ and with $C_2(CN)_4$ to give $[\{PtMe_3(\widehat{N\,N})\}_2\{\mu\text{-}N,C\text{-}C_2(CN)_4\}]$. The reactions are suggested to involve initial electrophilic attack on one of the mutually *trans* methylplatinum bonds (HX, $SO_2$) or electron transfer from a $\sigma$(PtC) orbital to the reagent $[C_2F_4, C_2(CN)_4]$.

## Introduction

The reactivity of methylplatinum(II) complexes towards electrophilic reagents and unsaturated reagents has been thoroughly studied, since such reactions are relevant to many catalytic processes involving square planar transition metal complexes [1–8]. The reagents, in many cases, attack the open platinum centre in the initial step and Pt–C bond cleavage occurs subsequently [1–8]. Most methylplatinum(IV) complexes are inert towards electrophiles, but it has now been found that the complexes $[PtMe_4(bipy)]$ and $[PtMe_4(phen)]$ where bipy = 2,2′-bipyridyl and phen = 1,10-phenanthroline [9, 10], are reactive towards electrophilic reagents and some unsaturated reagents. Previous studies of reactions of tetramethylplatinum(IV) complexes have been restricted to reductive eliminations from tertiary phosphine and arsine derivatives and ligand exchange in dimethylsulfide derivatives [10–12].

## Results and Discussion

The new reactions are summarized in the Scheme and NMR data for the products are in Table I.

Several of the new complexes were insufficiently stable to allow characterization by elemental analysis.

TABLE I. $^1$H NMR Spectra of $[PtMe_3X(\widehat{N\,N})]$.

| X | $\widehat{N\,N}$ | $\delta_1$[a] (ppm) | $^2J(PtH)_1$ (Hz) | $\delta_2$[b] (ppm) | $^2J(PtH)_2$ (Hz) | Solvent |
|---|---|---|---|---|---|---|
| Me[c] | bipy | 0.88 | 72 | −0.65 | 44 | $(CD_3)_2CO$ |
| Me[d] | phen | 1.03 | 72 | −0.65 | 44 | $(CD_3)_2CO$ |
| CN | bipy | 1.17 | 71 | −0.15 | 56 | $(CD_3)_2CO$ |
| $SO_2Me$[e] | bipy | 1.22 | 70 | 0.17 | 60 | $CDCl_3$ |
| SPh | bipy | 1.20 | 70 | 0.21 | 61 | $(CD_3)_2CO$ |
| OMe[f] | phen | 1.28 | 70 | 0.28 | 73.5 | $CD_3OD$ |
| OH | bipy | 1.32 | 71 | 0.47 | 74 | $(CD_3)_2CO$ |
| OPh | bipy | 1.60 | 69 | 0.56 | 75 | $C_6D_6$ |
| $OCOCH_3$[g] | phen | 1.39 | 70 | 0.30 | 75 | $CDCl_3$ |
| Cl | bipy | 1.22 | 70 | 0.39 | 75 | $CD_2Cl_2$ |
| $OCOCF_3$ | bipy | 1.24 | 68 | 0.45 | 78 | $CDCl_3$ |
| $OH_2$[h] | bipy | 1.24 | 68 | 0.67 | 82 | $(CD_3)_2CO$ |

[a]Subscript 1 refers to *Me*Pt *trans* to $\widehat{N\,N}$. [b]Subscript 2 refers to *Me*Pt *trans* to X. [c]bipy: δ 7.74 mult.; 8.19 mult.; 8.65 mult.; 8.94 mult. [d]phen: δ 8.03 mult.; 8.21 s.; 8.74 mult.; 9.23 mult. [e]$SCH_3$ δ 2.49 ppm, $^3J$(PtH) 4 Hz. [f]$OCH_3$ δ 3.32 ppm, exchanging with solvent. [g]$O_2CCH_3$ δ 1.61 ppm. [h]$[PtMe_3(OH_2)(bipy)]^+$ cation prepared as perchlorate salt; spectrum obtained at 5 °C.

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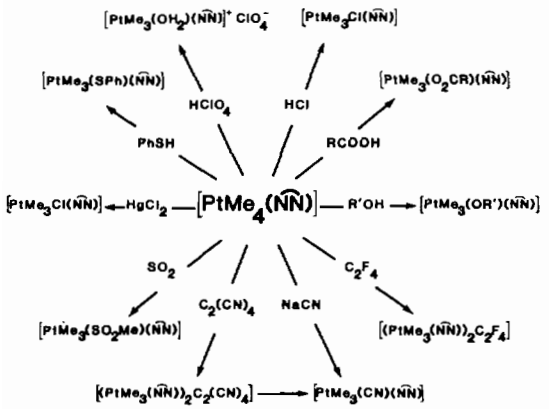
However, the NMR data are very characteristic and the nature of the donor atom X in $[PtMe_3XL_2]$ complexes determines the magnitude of the coupling constant $^2J(PtH)$ for the methylplatinum group *trans* to X (Table I) [9].

The complexes $[PtMe_4(bipy)]$ and $[PtMe_4(phen)]$ react with acids to give cleavage of one methylplatinum bond (Scheme 1). With the non-coordinating




NN = 2,2'-bipyridyl or 1,10-phenanthroline

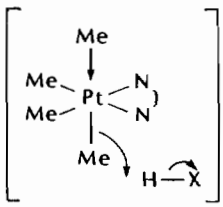
R = $CH_3$, $CF_3$

R' = H, $CH_3$, Ph

Scheme 1.

aqueous perchloric acid, the product was the aqua complex, *fac*-$[PtMe_3(OH_2)(bipy)][ClO_4]$, but all other acids HX gave *fac*-$[PtMe_3X(bipy)]$ or *fac*-$[PtMe_3X(phen)]$, where HX could be HCl, $CF_3CO_2H$, $CH_3CO_2H$, PhOH, PhSH, $H_2O$ or $CH_3OH$. Many of these products have been prepared earlier by Hall *et al.* [9], and all compounds were characterized by the $^1H$ NMR spectra (Table I). The complex $[PtMe_3(OMe)(phen)]$ acted as a strong base and reacted rapidly with solvents acetone or chloroform, in the latter case giving *fac*-$[PtMe_3Cl(phen)]$ as product. This is in contrast to the behaviour of the platinum(IV) methoxide cation, $[PtMe_2(OMe)(OH_2)(phen)]^+$, in which the Pt–OMe group is inert [13]. The remarkable difference in basicity is probably partly due to the present complex being neutral rather than cationic and also because the methoxide is *trans* to the strong $\sigma$-donor methyl group in the new complex. Both effects will lead to a greater negative charge on the alkoxide group.

The rates of reaction of the tetramethylplatinum(IV) complexes with acids were strongly dependent on acid strength and not on the co-ordinating ability of the group X in HX. The strong acids $HClO_4$, HCl and $CF_3CO_2H$ reacted very rapidly, whereas the weaker acids $CH_3CO_2H$, PhOH, PhSH, $H_2O$ and MeOH reacted slowly at room temperature. For example, a solution of $[PtMe_4(phen)]$ in methanol as solvent took about one week to react at room temperature, whereas reaction with a stoichiometric quantity of $HClO_4$ was complete within seconds. Similarly protonolysis of $[PtMe_4(bipy)]$ with $CF_3CO_2H$ ($pK_a$ 0.3) was complete within seconds at room temperature, but reaction with excess $CH_3CO_2H$ ($pK_a$ 4.8) required refluxing in acetone for one hour. These results suggest that initial protonation of the Pt–C bond occurs by an $S_E2$(open) mechanism to give $CH_4$ and $[PtMe_3(bipy)]^+$ or $[PtMe_3(phen)]^+$ followed by co-ordination of $X^-$ in a subsequent step. The high reactivity results from the high energy of the electrons in the $\sigma$(Pt–C) bonds for the mutually *trans* methyl groups or, expressed in another way, to the high *trans*-influence of the methyl group *trans* to the Pt–C bond being cleaved (Structure **1**) [14, 15].




**1**

A brief kinetic study of the reaction of $[PtMe_4(bipy)]$ with PhSH in acetone-$d_6$ solvent was carried out, with monitoring by $^1H$ NMR spectroscopy. In this way, both disappearance of $[PtMe_4(bipy)]$ and appearance of $[PtMe_3(SPh)(bipy)]$ could be followed independently. Using a large excess of PhSH, the reactions followed good first order kinetics and the observed first order rate constants were directly proportional to the concentration of PhSH (Fig. 1). Thus the rate law was established as:

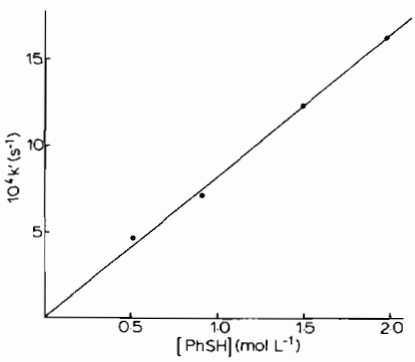


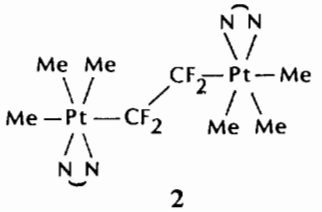

Fig. 1. Dependence of observed first order rate constants, $k'$, for reaction of $[PtMe_4(bipy)]$ with excess PhSH in acetone-$d_6$ at 36 °C on the concentration of PhSH.

$$\frac{-d}{dt}[PtMe_4(bipy)] = \frac{d}{dt}[PtMe_3(SPh)(bipy)] = k_2[PtMe_4(bipy)][PhSH]$$

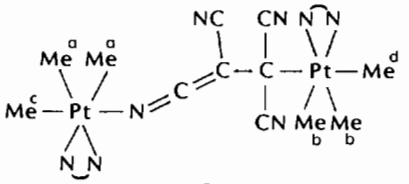
The second order rate constant $k_2 = 8.2 \times 10^{-4}$ L mol$^{-1}$ s$^{-1}$ at 36 °C. These results are clearly consistent with the mechanism proposed above, with the intermediate or transition state of structure **1**. In contrast, PhSH reacts with methylplatinum(II) complexes by a free radical chain mechanism [4]. Such a mechanism requires a vacant site at the metal centre and is not possible with [$PtMe_4$(bipy)], which is coordinatively saturated.

[$PtMe_4$(bipy)] fails to react with unsaturated reagents, such as carbon monoxide, which must first coordinate to the metal centre prior to migratory insertion. Similarly, $CO_2$, $CS_2$ and dimethyl maleate failed to insert into PtMe bonds. The only simple insertion reaction we have discovered is the reaction of $SO_2$ to give the S-sulfinate derivative *fac*-[$PtMe_3$-($SO_2$Me)(bipy)]. This product was characterized as the S-sulfinate by the IR spectrum [$\nu(SO_2)$ at 1150 and 1045 cm$^{-1}$] [16], and by the NMR spectrum, which indicated a methylplatinum group *trans* to sulfur [$^2J$(PtH) 60 Hz, Table I] and the presence of $MeS(=O)_2Pt$ resonanace with coupling to $^{195}$Pt [δ(MeS) 2.49 ppm, $^3J$(PtH) 4 Hz]. Other co-ordinatively saturated transition metal alkyls are known to react with $SO_2$ and an ionic pair intermediate, in the present case [$PtMe_3$(bipy)]$^+$[Me-$SO_2$]$^-$, is invoked [16].

The activated alkenes $C_2F_4$ and $C_2(CN)_4$ reacted with [$PtMe_4$(phen)] or [$PtMe_4$(bipy)] to give [{Pt-$Me_3$(phen)}$_2C_2F_4$] or [{$PtMe_3$(bipy)}$_2C_2(CN)_4$] respectively, but these complexes had different structures. The $C_2F_4$ complex is characterized as having structure **2**, $\widehat{NN}$ = phen. The $^1$H NMR spectrum



**2**



**3**

contained two methylplatinum resonances in a 2:1 ratio, as expected, and the lower intensity resonance had a low coupling constant $^2J(PtCH_3)$ = 48 Hz indicating that this methyl group was *trans* to a carbon donor ligand (Table I). The $^{19}$F NMR spectrum contained a singlet with $^{195}$Pt satellites, showing that all fluorine atoms are equivalent. Irradiation of this dimer in $CDCl_3$ gave a mixture of [$PtMe_3$Cl(phen)] and a second product tentatively assigned as [{$PtMe_2$Cl(phen)}$_2C_2F_4$]. In contrast, The $^1$H NMR spectrum of the $C_2(CN)_4$ product (Fig. 2) indicated structure **3**, $\widehat{NN}$ = bipy. The spectrum contained four MePt resonances in the

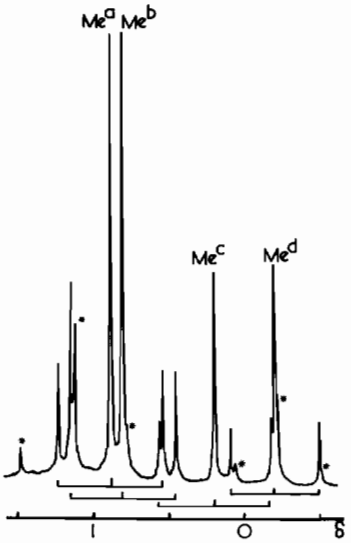



Fig. 2. $^1$H NMR spectrum in the MePt region of [($PtMe_3$-bipy)$_2C_2(CN)_4$)]. For nomenclature, see structure **3**. Peaks labelled asterisk are due to the decomposition product [$PtMe_3$(CN)(bipy)]. $^{195}$Pt satellites of the resonances due to **3** are shown below.

ratio 2:2:1:1, indicating non-equivalent *fac*-$Me_3Pt$ units in the dimer. The peaks of intensity 2 correspond to MePt groups *trans* to bipy and have coupling constants $^2J$(PtH) = 70 Hz. The peaks of intensity 1 have very different coupling constants $^2J$(PtH) = 58 Hz and 74 Hz, and are assigned as being *trans* to carbon and nitrogen donor atoms respectively [9]. Therefore the structure **3** with $C_2(CN)_4$ as a C, N-bridging ligand is proposed. Previously, insertion of $C_2(CN)_4$ into M–H or M–R bonds (R = alkyl) has given complexes with functional groups M–N=C=C(CN)C(CN)$_2$H or M–N=C=C(CN)C-(CN)$_2$R respectively [17, 18]. The IR spectra in the 2000 cm$^{-1}$ region of these complexes are very similar to those of the present complex **3** [$\nu$, 2190 cm$^{-1}$ (s), 2160 cm$^{-1}$, 1955 cm$^{-1}$ (w)], giving further support to the proposed structure. Complex **3** decomposed in solution to give [$PtMe_3$(CN)(bipy)],

which was prepared independently as shown in the Scheme.

The fate of the fourth methylplatinum group in these reactions with $C_2F_4$ and $C_2(CN)_4$ is unclear. The reaction with $C_2(CN)_4$ gave not only the buff-coloured complex **3**, but also very intensely coloured blue and red species, which could not be separated completely by column chromatography. NMR spectra of the crude product mixture gave extra methyl resonances around $\delta$ 2 ppm, which we tentatively suggest arise from methyl groups combining with $C_2(CN)_4$. The data are most readily interpreted in terms of combination of $[PtMe_3(\widehat{N\,N})]$ radicals with $C_2F_4$ or $C_2(CN)_4$, after homolysis of a Pt–Me bond of $[PtMe_4(\widehat{N\,N})]$. Since only alkenes with very electronegative substituents are reactive, it is likely that reaction is initiated by electron transfer from the $\sigma$(Pt–C) level, which is expected to be the HOMO, to the alkene [19].

## Experimental

$[PtMe_4(phen)]$ and $[PtMe_4(bipy)]$ were prepared as reported previously [10]. $^1$H NMR spectra were recorded on Varian T60, XL-100 and XL-200 instruments. Electronic spectra were recorded on a Cary 118 UV–visible spectrometer and infrared spectra on a Beckman IR4250. Elemental analyses were carried out by Guelph Chemical Laboratories.

*Reaction with $HClO_4$*

A solution of $HClO_4$ (1 ml, 1%) in MeOH was added to a stirred solution of $[PtMe_4(bipy)]$ (49 mg) in acetone (10 ml). The solution turned colourless immediately; stirring was continued for 10 min. An off-white solid was recovered (48 mg) and identified by $^1$H NMR [9] as $[PtMe_3(H_2O)(bipy)][ClO_4]$.

*Reaction with HCl*

$[PtMe_4(bipy)]$ (52 mg) was dissolved in a mixture of $CH_2Cl_2$ (12 ml) and MeOH (3 ml). Acetyl chloride (9 $\mu$l) was added and the mixture was stirred until the orange colour disappeared (5 min). A white solid was recovered (46 mg) and identified by $^1$H NMR [9] as $[PtMe_3Cl(bipy)]$. M.p. 230 °C, decomp. *Anal.* Calc. for $[PtMe_3Cl(bipy)]$: C, 36.1; H, 3.94; N, 6.5. Found: C, 36.1%; H, 4.2; N, 6.7%.

*Reaction with $CF_3COOH$*

$[PtMe_4(bipy)]$ (50 mg) was dissolved in acetone (10 ml). $CF_3COOH$ (9 $\mu$l) was added and the solution decolourized immediately. A beige solid (52 mg) was recovered and identified by $^1$H NMR as $[PtMe_3(OCOCF_3)(bipy)]$.

*Reaction with $CH_3COOH$*

$[PtMe_4(phen)]$ (60 mg) was combined with glacial acetic acid (30 $\mu$l) in acetone (10 ml) and refluxed until the solution turned pale yellow (~1 h). An off-white solid (58 mg) was recovered and identified by $^1$H NMR [9] as $[PtMe_3(OCOCH_3)(phen)]$, m.p. 220–225 °C decomp.

*Reaction with Phenol*

$[PtMe_4(bipy)]$ (50 mg) was dissolved in acetone (15 ml) and phenol (100 mg) was added. The solution was refluxed for several hours and then pumped to dryness. The resultant solid was dissolved in benzene and the excess PhOH was extracted with water. The yellow solid recovered from the organic phase was identified by $^1$H NMR as $[PtMe_3(OPh)(bipy)]$.

*Reaction with Water*

A solution of $[PtMe_4(phen)]$ (50 mg) in acetone (10 ml) was treated with $H_2O$ (2 ml) and heated to 50 °C for 2 weeks. Some general decomposition occurred. The major product was a white solid, identified by $^1$H NMR as $[PtMe_3(OH)(phen)]$ [9].

*Reaction with MeOH*

$[PtMe_4(phen)]$ (50 mg) was dissolved in MeOH (50 ml) and allowed to stand until completely decolourized (1 wk, R.T.). The off-white solid recovered from the solution was identified by $^1$H NMR as $[PtMe_3(OMe)(phen)]$. M.p. 65–75 °C decomp. The compound decomposes on exposure to moist air.

*Reaction with PhSH*

A solution of $[PtMe_4(bipy)]$ (10 mg) in benzene (2 ml) was treated with PhSH (0.10 ml) and allowed to stand at room temperature overnight. The product was recovered as bright yellow needles and identified by $^1$H NMR as $[PtMe_3(SPh)(bipy)]$. M.p. 160–170 °C decomp. *Anal.* Calc. for $[PtMe_3(SPh)(bipy)]$: C, 45.1; H, 4.36; N, 5.54. Found: C, 44.8; H, 4.45; N, 5.53%.

Kinetic studies of this reaction were carried out by using $^1$H NMR spectrometry to monitor the reactions. Samples of $[PtMe_4(bipy)]$ in acetone-d$^6$ were allowed to react with a large excess of PhSH within the thermostatted (309 K) T-60 spectrometer. Individual thiol concentrations, observed first order rate constants, $k'$: 0.505 mol l$^{-1}$, 4.71 × 10$^{-4}$ s$^{-1}$; 0.916 mol l$^{-1}$, 7.17 × 10$^{-4}$ s$^{-1}$; 1.49 mol l$^{-1}$, 1.23 × 10$^{-3}$ s$^{-1}$; 1.98 mol l$^{-1}$; 1.63 × 10$^{-3}$ s$^{-1}$.

*Reaction with $HgCl_2$*

A solution of $[PtMe_4(bipy)]$ (12 mg) in acetone (1 ml) was treated with a solution of $HgCl_2$ (10 mg) in acetone (1 ml). The solution immediately decolourized and a white precipitate formed. The product was identified by $^1$H NMR [9] and mass spectrometry as $[PtMe_3Cl(bipy)]$.

*Reaction with NaCN*

$[PtMe_4(bipy)]$ (50 mg) was dissolved in dry acetone and added to a mixture of NaCN (6 mg) in dry EtOH (40 ml). More EtOH was added until the NaCN was completely dissolved and the solution was stirred at room temperature until it had decolourized (18 h). A beige solid was recovered and identified by $^1H$ NMR [9] as $[PtMe_3(CN)(bipy)]$. Infrared absorption: $\nu(C{\equiv}N)$ = 2125 $cm^{-1}$ (s). M.p. 200–220 °C decomp.

*Reaction with $SO_2$*

$[PtMe_4(bipy)]$ (50 mg) was dissolved in $CH_2Cl_2$ (10 ml) and treated with a stream of $SO_2$ (g). The solution turned pale yellow almost immediately. An off-white solid (30 mg) was recovered and identified by $^1H$ NMR as $[PtMe_3(SO_2Me)(bipy)]$. M.p. 210–230 °C decomp.

*Reaction with $C_2F_4$*

$[PtMe_4(phen)]$ (50 mg) was dissolved in dry acetone. The solution was degassed, an equimolar amount of $C_2F_4$ (g) was condensed into the flask and it was sealed. The flask was placed in an oven at 50 °C until the solution decolourized (2 weeks). An off-white solid was recovered which was identified as $[(PtMe_3(phen))_2C_2F_4]$. NMR in $(CD_3)_2CO$: –0.40 ppm [$^2J$(PtH) 48 Hz, *Me*Pt *trans* to $C_2F_4$]; 1.04 ppm [$^2J$(PtH) 72 Hz, *Me*Pt *trans* to phen]; –114.0 ppm [$^2J$(PtF) 207 Hz, $^{19}F$]. *Anal.* Calc. for $[\{PtMe_3(phen)\}_2C_2F_4]$: C, 37.67; H, 3.81; N, 6.28. Found: C, 37.58; H, 4.15; N, 5.91%. Photolysis of this dimer in $CDCl_3$ with a mercury lamp filtered at 350 nm produced a mixture of $[PtMe_3Cl(phen)]$ and a second compound assigned as $[\{PtMe_2Cl(phen)\}_2C_2F_4]$. NMR in $CDCl_3$: 1.59 ppm [$^2J$(PtH) 70 Hz, *Me*Pt *trans* to phen]; –136.8 ppm [$^2J$(PtF) 382 Hz, $^{19}F$].

*Reaction with $C_2(CN)_4$*

Solutions of $[PtMe_4(bipy)]$ (100 mg) and tetracyanoethylene (15 mg) in acetone were prepared and chilled in an acetone/$CO_2$(s) bath. The two solutions were combined and mixed thoroughly then allowed to warm to room temperature. The resulting dark purple solution was pumped to dryness and the desired product was separated from a number of coloured impurities by preparative TLC. The product, a beige solid, was identified by $^1H$ NMR as $[(PtMe_3(bipy))_2C_2(CN)_4]$, **3**. This dimer converts to $[PtMe_3(CN)(bipy)]$ either in the solid state or in acetone solution, and we were unable to obtain satisfactory analytical data. NMR in $(CD_3)_2CO$: –0.18 ppm [$^2J$(PtH) 58 Hz, *Me*Pt *trans* to $C_2(CN)_4$]; 0.20 ppm [$^2J$(PtH) 74 Hz, *Me*Pt *trans* to $C_2(CN)_4$]; 0.81, 0.89 ppm [$^2J$(PtH) 70 Hz; *Me*Pt *trans* to bipy]. IR: 2190(s), 2160(sh), 1955(w) [$\nu$(CN) and $\nu$(N=C=C)].

**Acknowledgement**

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