

A Novel Oxidative Addition Product from $[Pt_2(dba)_3]$: Synthesis and Spectroscopic Characterization of a Bimetallic Pt- η^2 -Tetracyanoethylene Complex Containing 2,3,5,6-Tetrakis(α -pyridyl)pyrazine

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$\{[Pt(\eta^2\text{-TCNE})_2(\mu\text{-TPP})]\}$ (**1**) foi preparado a partir da reação entre o composto de Pt(0) $[Pt_2(dba)_3]$ (dba = dibenzilidenoacetona), tetracianoetileno (TCNE) e 2,3,5,6-tetraquis(α -piridil)pirazina (TPP) na razão estequiométrica 1:2:1, respectivamente. **1** foi caracterizado por análise elementar, espectroscopia no infravermelho, RMN de 1H em solução e RMN de ^{13}C no estado sólido (CP/MAS). De acordo com os espectros de RMN, o ligante TPP em **1** se coordena a cada centro metálico por dois átomos de nitrogênio piridínicos, segundo um modo de coordenação bis-bidentado já relatado em outros complexos de TPP com Pt^{II}. Além dos sinais atribuídos aos átomos de carbono do TPP (δ 128-155) e aos átomos de carbono dos grupos nitrila (δ 115,1), o espectro de RMN de ^{13}C -CP/MAS de **1** exibe na região de menor frequência um duplo duplete [δ_1 -2,6; $^1J(^{195}Pt\text{-}^{13}C) = 223$ Hz e δ_2 1,6; $^1J(^{195}Pt\text{-}^{13}C) = 188$ Hz]. Estes últimos sinais são atribuídos aos átomos de carbono etilênicos do TCNE ligados a platina e confirmam que a ligação nos fragmentos Pt- η^2 -TCNE é melhor descrita segundo o modelo metalaciclopropano.

$\{[Pt(\eta^2\text{-TCNE})_2(\mu\text{-TPP})]\}$ (**1**) has been prepared from the Pt(0) compound $[Pt_2(dba)_3]$ (dba = dibenzylideneacetone), tetracyanoethylene (TCNE), and 2,3,5,6-tetrakis(α -pyridyl)pyrazine (TPP) in the 1:2:1 stoichiometric ratio, respectively. **1** has been characterized by elemental analysis, infrared spectroscopy, solution 1H NMR and solid-state ^{13}C (CP/MAS) NMR spectroscopy. According to the NMR spectra of **1**, TPP binds to each metal through two pyridine nitrogen atoms. In addition to the signals assigned to the TPP carbon atoms (δ 128-155) and to the nitrile carbon atoms (δ 115.1), the ^{13}C -CP/MAS NMR spectrum of **1** exhibits a double doublet [δ_1 -2.6, $^1J(^{195}Pt\text{-}^{13}C) = 223$ Hz and δ_2 1.6, $^1J(^{195}Pt\text{-}^{13}C) = 188$ Hz] in the low frequency region. These signals are assigned to the ethylenic TCNE carbon atoms attached to platinum and confirm that the bonding at the Pt- η^2 -TCNE moieties is best described according to the metalacyclopropane model.

Keywords: organoplatinum chemistry, bimetallic complexes, nitrogen heterocyclic ligand, ^{13}C -CP/MAS

Introduction

2,3,5,6-Tetrakis(α -pyridyl)pyrazine (TPP) is a heterocyclic ligand containing six potentially coordinating nitrogen sites. The ability of TPP to bind transition and main-group metals has been the subject of a number of studies.¹⁻²⁰ To date, seven different chelating modes have been described for TPP (Figure 1). Among them, the tridentate modes are by far the most abundant ones. The variety of coordination modes of TPP can be accounted

for by the free rotation about the four pyridine-pyrazine linkages. In effect, recent *ab initio* calculations at the RHF/6-31++G(d,p) level have shown the existence of 14 conformers of TPP with low-energy interconversion barriers.²¹

The few examples of platinum-TPP complexes involve Pt^{II} and have revealed that the chelating mode adopted by TPP depends upon the reacted Pt^{II} species.^{7,10} The reaction between TPP and *trans*- $[Pt(PEt_3)Cl_2]$ has afforded the isolation of the bimetallic cation $\{[Pt(PEt_3)Cl_2(\mu\text{-TPP})]\}^{2+}$, in which TPP acts as a bis-bidentate(A) (Figure 1) chelating ligand.⁷ As another example, the reaction

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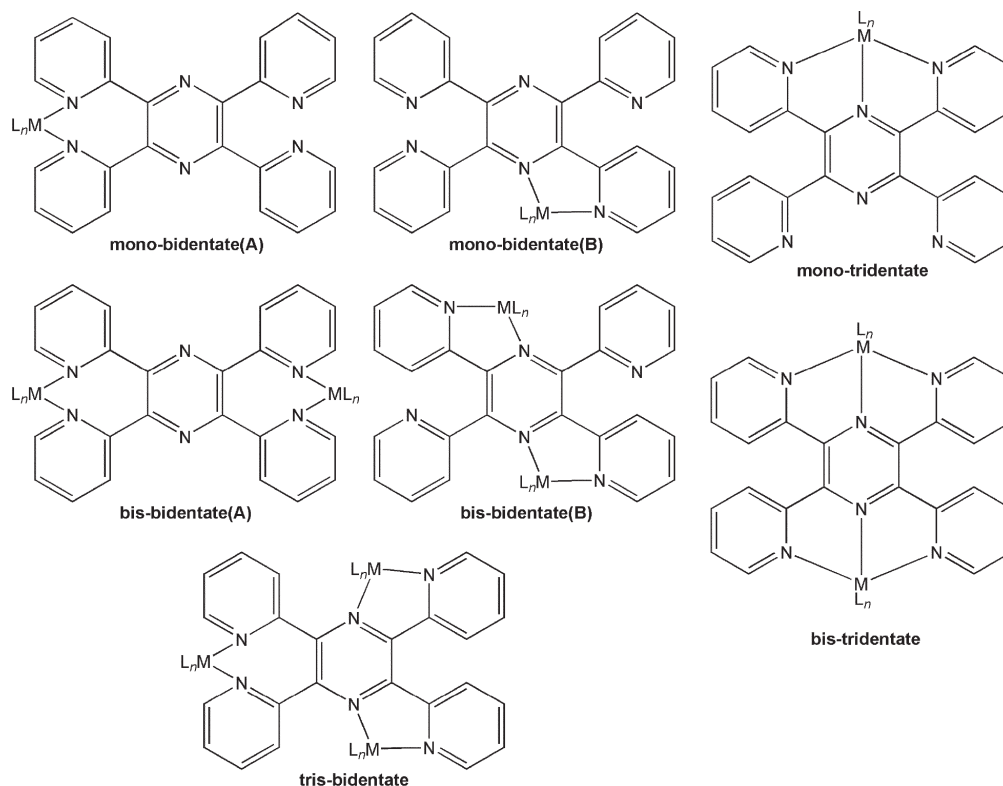


Figure 1. The chelating modes of TPP.

between TPP and *cis*-[Pt(DMSO)₂Cl₂] has yielded the complex salt [{PtCl₂}(μ-TPP)][Pt(DMSO)Cl₃]₂.¹⁰ In this latter case, TPP bridges the Pt^{II} centers according to the bis-tridentate coordination mode. Such interesting examples along with the paucity of studies concerning the reactivity and coordinating behavior of TPP toward organoplatinum reagents have prompted us to undertake the reaction between TPP and the formally Pt(0) reagent [Pt₂(dba)₃] (dba = dibenzylideneacetone).

A well-known strategy to synthesize Pt-η²-alkene complexes with N,N donor ligands, such as α-diimines or aromatic nitrogen heterocycles, involves a “one-pot” reaction between a zerovalent platinum reagent [*e.g.* [Pt₂(dba)₃] or [Pt(1,5-cyclooctadiene)₂], an olefin with electron withdrawing groups, such as tetracyanoethylene (TCNE), and the N,N donor ligand.²²⁻²³ Usually, the isolated products have the general formula [Pt(η²-alkene)(N,N)] and the bonding at the Pt-η²-alkene moiety is described according to the metallocyclopropane model.²⁴ Indeed, in olefin complexes of platinum, the bonding at the Pt-η²-alkene moiety can be understood in terms of either the classical Dewar-Chatt-Duncanson model^{24,25} or the metallocyclopropane model.²⁴ Spectroscopic methods and single-crystal X-ray diffraction studies have been used to distinguish between these two bonding possibilities in Pt-η²-alkene structures.²²⁻²⁶ In this work we have employed

the aforementioned strategy to prepare a bimetallic Pt-η²-TCNE complex containing TPP as a bis-bidentate ligand, namely [{Pt(η²-TCNE)}₂(μ-TPP)] (**1**). Solid-state ¹³C (CP/MAS) NMR spectroscopy has been used to examine the bonding at the Pt-η²-TCNE moieties as well as the mode adopted by TPP upon coordination to the metallic centers.

Experimental

General details

The reaction and the work-up of the reaction mixture were carried out under argon using Schlenk-type glassware and vacuum-inert gas line manipulation techniques. THF was dried over sodium-benzophenone ketyl and deoxygenated according to standard techniques. [Pt₂(dba)₃]²⁷ and TPP²⁸ were synthesized according to the literature methods. TCNE was purchased from Acros and used as received. CD₃CN (Cambridge Isotopes, Inc.) was commercially obtained and stored over 3 Å molecular sieves.

Physical measurements

Elemental analysis (C, H, and N) was performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. IR spectra

were recorded on a Magna-IR760 FTIR Nicolet spectrometer. The spectra were obtained using Nujol mulls between CsI windows (4000-200 cm⁻¹) and a resolution of 4 cm⁻¹. ¹H (CD₃CN) and solid-state ¹³C (CP/MAS) NMR spectra were acquired from Bruker DPX200 (¹H) and DRX300 (¹³C) instruments operating at 200.08 MHz (¹H) and at 75.47 MHz (¹³C), respectively. All NMR studies were performed at 293 K, and the chemical shift (δ / ppm) values were determined in relation to SiMe₄. In the ¹³C-CP/MAS NMR spectra the samples were spun at 6-8 kHz in 4 mm diameter ZrO₂ rotors with Kel-F caps. A satisfactory ¹³C-CP/MAS NMR spectrum for **1** was obtained using a relaxation delay of 20 s and a contact time of 1 ms. A ¹³C-CP/MAS NMR spectrum of TPP with good signal to noise ratio was obtained with a contact time of 0.5 ms and a relaxation delay of 60 s.

Preparation of $\{[Pt(\eta^2\text{-TCNE})]_2(\mu\text{-TPP})\}$ (**1**)

A deep purple solution of [Pt₂(dba)₃] (0.115 g, 0.10 mmol) and TCNE (0.044 g, 0.34 mmol) in THF (10 mL) was stirred at room temperature (r.t.) for 30 min. Then, solid TPP (0.030 g, 0.08 mmol) was slowly added to this solution with constant magnetic stirring. The resulting mixture was stirred at r.t. for 22 h. After this period, a brown solid was filtered off, washed with CH₂Cl₂ (4 x 5 mL) and dried under vacuum. Yield: 0.062 g (78%). The product is slightly hygroscopic and sparingly soluble in most organic solvents but readily decomposes in DMF and DMSO.

Data for 1. mp: infusible to 300 °C. Anal. Calc. for C₃₆H₁₆N₁₄Pt₂·2H₂O: C, 40.38; H, 1.89; N, 18.32%. Found: C, 40.08; H, 1.81; N, 18.69%. FT-IR (nujol mull) ν_{max} /cm⁻¹: ν (CH)_{TPP}, 3109 (w), 3078 (w), 3053 (w); ν (CN)_{TCNE}, 2228 (m), 2201 (sh); ν (CC/CN)_{TPP}, 1605 (m), 1568 (w), 1487 (w), 1457 (s), 1388 (m); δ (CH)_{TPP}, 784 (m), 759 (m); ν (Pt-C), 385 (m), 375 (m); ν (Pt-N), 280 (m), 246 (s). ¹H NMR (CD₃CN), δ / ppm: 8.97 (4H, dd, H6); 8.11 (4H, m, H4); 7.99 (4H, dd, H3); 7.74 (4H, m, H5). ¹³C-CP/MAS,

δ_{max} /ppm (isotropic signals): 155.0 (C2_{pz}); 151.2 (C2_{py}+C6); 140.2 (C3); 128.2 (C4+C5); 115.1 (nitrile groups); δ_1 -2.6 [d, ¹J(¹⁹⁵Pt-¹³C) = 223 Hz] and δ_2 1.6 [d, ¹J(¹⁹⁵Pt-¹³C) = 188 Hz] (ethylenic carbon atoms attached to Pt). For these two latter signals, δ_1 (ν_A) and δ_2 (ν_B), $\Delta\nu = [(v_1 - v_4)(v_2 - v_3)]^{1/2} = 317$ Hz, which is approximately equal to 1.6 *J*, considering *J* \cong 200 Hz. The atom numbering is shown in Figure 3. Here, H3 is the H atom bound to C3 *etc.* Owing to the low solubility of **1** in most organic solvents, its ¹³C{¹H} NMR spectrum in solution could not be measured. Attempts to grow suitable single crystals of **1** for X-ray diffraction studies were unsuccessful.

Results and Discussion

Selected FT-IR data for [Pt₂(dba)₃], TCNE, TPP, and **1** are listed in Table 1. The FT-IR spectrum of **1** does not exhibit bands in the expected carbonyl region, thereby indicating that the dba ligands in the zerovalent platinum reagent were displaced in the reaction conditions. Moreover, the bands assigned to the nitrile groups of **1** were shifted to lower wavenumbers with respect to free TCNE. Table 1 also shows that some TPP internal vibrations were shifted to lower wavenumbers (*e.g.* 1457 and 1388 cm⁻¹) upon complexation; others, however, were shifted to higher wavenumber values (*e.g.* 1605 cm⁻¹), whereas some other bands remained unchanged (*e.g.* 1568 and 1487 cm⁻¹). In the low-frequency region of the FT-IR spectrum of **1**, the bands at 385, and 375 cm⁻¹ are assigned to the ν (Pt-C) stretching modes, whereas the bands at 280 and 246 cm⁻¹ are ascribed to the ν (Pt-N) vibration modes.²⁹

Selected ¹H NMR data for TPP and for **1** are summarized in Table 2. According to the number of ¹H signals and their integration (see Experimental Section), it is possible to suggest that there are no uncoordinated pyridine rings in **1**. This result implies that in **1** TPP is coordinated to the platinum centers according to the bis-bidentate(A) chelating mode. The structure proposed for **1** is illustrated in Figure 2. In Table 2 the $\Delta\delta$ values show

Table 1. Selected FT-IR data (cm⁻¹) for [Pt₂(dba)₃], TCNE, TPP, and **1**^{a,b}

	ν (C=O)	ν (CN) _{nitrile}	ν (CC/CN)	δ (CH)
[Pt ₂ (dba) ₃]	1711 (m), 1628 (s)	-	-	-
TCNE	-	2258 (s), 2220 (s)	c	-
TPP	-	-	1587 (s), 1566 (s), 1486 (w), 1476 (m), 1434 (m), 1392 (s)	807 (s), 784 (s), 753 (s)
1	-	2228 (m), 2201 (sh)	1605 (m), 1568 (w), 1487 (w), 1457 (s), 1388 (m)	784 (m), 759 (m)

^ash = shoulder, w = weak, m = medium, s = strong; ^bspectra obtained in nujol mull between CsI windows; ^cnot uniquely assignable.

that the signals for H4, H5, and H6 were shifted to higher frequencies on coordination, whereas the signal for H3 exhibited only a slight shift to lower frequency.

Table 2. Selected solution ^1H NMR data (δ / ppm) for TPP and for **1**^{a,b}

	TPP	1	$\Delta\delta$
H3	8.05 (dd)	7.99 (dd)	0.06
H4	7.80 (m)	8.11 (m)	-0.31
H5	7.24 (m)	7.74 (m)	-0.50
H6	8.39 (dd)	8.97 (dd)	-0.58

^aspectra obtained in CD_3CN ; ^bdd = double doublet, m = multiplet.

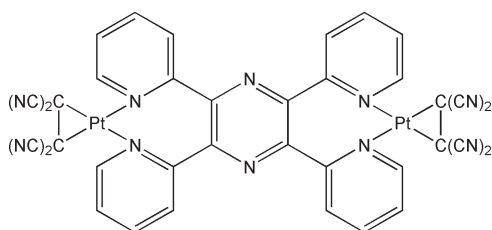


Figure 2. Structure proposed for **1**.

The ^{13}C -CP/MAS NMR spectrum of **1** is depicted in Figure 3. The signals in the δ 128–155 ppm range are assigned to the TPP carbon atoms. In the ^{13}C -CP/MAS NMR spectrum of free TPP, these signals appear in the region from 124 to 160 ppm.²⁰ The signal at δ_{max} 115.1 (Figure 3) is attributed to the nitrile carbon atoms. In the solution (CDCl_3) ^{13}C NMR spectrum of free TCNE, a single nitrile signal can be seen at 117 ppm. Also in the solution ^{13}C NMR spectrum of free TCNE, the signal for the olefinic carbon atoms lies at δ 101. In the ^{13}C NMR spectrum of **1** (Figure 3) no signals were observed in the expected alkene $\text{C}(sp^2)$ region.³⁰ Instead, a double doublet appears at lower frequencies, *e.g.* in the alkane $\text{C}(sp^3)$ region.³⁰ These signals, δ_1 – 2.6 [$^1J(^{195}\text{Pt}-^{13}\text{C}) = 223$ Hz] and δ_2 1.6 [$^1J(^{195}\text{Pt}-^{13}\text{C}) = 188$ Hz] (C^a in Figure 3), are assigned to the TCNE carbon atoms bound to platinum. The presence of these two isotropic signals, δ_1 and δ_2 , is likely to indicate that the asymmetric unit of **1** bears two crystallographically distinct coordinated carbon atoms of TCNE.³¹ Moreover, the low values for the $^1J(^{195}\text{Pt}-^{13}\text{C})$ coupling constants in **1** are in agreement with literature data for related compounds.²⁶

The very low δ_1 and δ_2 values (Figure 3) imply that the TCNE carbon atoms attached to platinum exhibit an approximate sp^3 character. This confirms that the bonding at the $\text{Pt}-\eta^2\text{-TCNE}$ moieties is best described in terms of the metalacyclopropane model,²⁴ as illustrated in Figure 2. Hence, to each platinum in **1** one might assign a 2+ formal oxidation state. Indeed, the reaction described

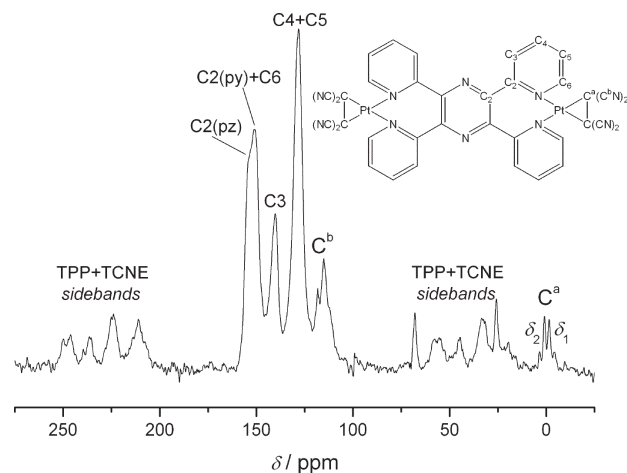


Figure 3. The ^{13}C -CP/MAS NMR spectrum of **1**. Spectrum recorded at a spinning frequency of 7.2 kHz.

herein can be thought of as resulting from the oxidative addition of the olefinic $\text{C}=\text{C}$ bond of TCNE to $\text{Pt}(0)$ in the presence of TPP.

Conclusions

The reaction between $[\text{Pt}_2(\text{dba})_3]$, TCNE, and TPP, in the 2:2:1 (Pt:TCNE:TPP) stoichiometric ratio, gave the bimetallic heteroleptic product $[\{\text{Pt}(\eta^2\text{-TCNE})\}_2(\mu\text{-TPP})]$ (**1**). **1** was characterized by several spectroscopic techniques, including solid-state ^{13}C (CP/MAS) NMR spectroscopy. The solution ^1H NMR spectrum of **1** provided convincing evidence that TPP is bound to the Pt atoms according to the bis-bidentate(A) coordination mode. The ^{13}C -CP/MAS NMR spectrum of **1** confirmed that the bonding at the $\text{Pt}-\eta^2\text{-TCNE}$ moieties is described in terms of the expected metalacyclopropane model.

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References

- Vogler, L. M.; Scott, B.; Brewer, K. J.; *Inorg. Chem.* **1993**, *32*, 898.
- Graf, M.; Greaves, B.; Stoeckli-Evans, H.; *Inorg. Chim. Acta* **1993**, *204*, 239.
- Vogler, L. M.; Brewer, K. J.; *Inorg. Chem.* **1996**, *35*, 818.
- Graf, M.; Stoeckli-Evans, H.; Escuer, A.; Vicente, R.; *Inorg. Chim. Acta* **1997**, *257*, 89.
- Lee, J. D.; Vrana, L. M.; Bullock, E. R.; Brewer, K. J.; *Inorg. Chem.* **1998**, *37*, 3575.

6. Hartshorn, C. M.; Daire, N.; Tondreau, V.; Loeb, B.; Meyer, T. J.; White, P. S.; *Inorg. Chem.* **1999**, *38*, 3200.
7. Teles, W. M.; Speziali, N. L.; Filgueiras, C. A. L.; *Polyhedron* **2000**, *19*, 739.
8. Chen, X.; Femia, F. J.; Babich, J. W.; Zubieta, J.; *Inorg. Chim. Acta* **2001**, *315*, 66.
9. Bera, J. K.; Campos-Fernández, C. S.; Rodolphe, C.; Bunbar, K. R.; *Chem. Commun.* **2002**, 2536.
10. Sakai, K.; Kurashima, M.; *Acta Cryst.* **2003**, *E59*, m411.
11. Lalrempuia, R.; Govindaswamy, P.; Mozharivskyj, Y. A.; Kollipara, M. R.; *Polyhedron* **2004**, *23*, 1069.
12. Fantacci, S.; de Angelis, F.; Wang, J.; Bernhard, S.; Selloni, A.; *J. Am. Chem. Soc.* **2004**, *126*, 9715.
13. Maekawa, M.; Minematsu, T.; Konaka, H.; Sugimoto, K.; Kuroda-Sowa, T.; Suenaga, Y.; Munakata, M.; *Inorg. Chim. Acta* **2004**, *357*, 3456.
14. Carranza, J.; Sletten, J.; Brennan, C.; Lloret, F.; Cano, J.; Julve, M.; *J. Chem. Soc., Dalton Trans.* **2004**, 3997.
15. Bitzer, R. S.; Filgueiras, C. A. L.; Lopes, J. G. S.; Santos, P. S.; Herbst, M. H.; *Transit. Met. Chem.* **2005**, *30*, 636.
16. Hadadzadeh, H.; Rezvani, A. R.; Yap, G. P. A.; Crutchley, R. J.; *Inorg. Chim. Acta* **2005**, *358*, 1289.
17. Bitzer, R. S.; Teles, W. M.; Abras, A.; Ardisson, J. D.; Filgueiras, C. A. L.; *J. Braz. Chem. Soc.* **2005**, *16*, 963.
18. Hsu, G. Y.; Chen, C. W.; Cheng, S. C.; Lin, S. H.; Wei, H. H.; Lee, C. J.; *Polyhedron* **2005**, *24*, 487.
19. Morsali, A.; Ramazani, A.; *Z. Anorg. Allg. Chem.* **2005**, *631*, 1759.
20. Bitzer, R. S.; Pereira, R. P.; Rocco, A. M.; Lopes, J. G. S.; Santos, P. S.; Nascimento, M. A. C.; Filgueiras, C. A. L.; *J. Organomet. Chem.* **2006**, *691*, 2005.
21. Padgett, C. W.; Pennington, W. T.; Hanks, T. W.; *Cryst. Growth Des.* **2005**, *5*, 737.
22. van Asselt, R.; Elsevier, C. J.; Smeets, W. J. J.; Spek, A. L.; *Inorg. Chem.* **1994**, *33*, 1521.
23. Tromp, D. S.; Duin, M. A.; Kluwer, A. M.; Elsevier, C. J.; *Inorg. Chim. Acta* **2002**, *327*, 90.
24. Crabtree, R. H.; *The Organometallic Chemistry of the Transition Metals*; 4th Ed.; Wiley-Interscience: New Jersey, 2005, pp. 125-131.
25. Dewar, M. J. S.; *Bull. Soc. Chim. Fr.* **1951**, *18*, 79; Chatt, J.; Duncanson, L. A.; *J. Chem. Soc.* **1953**, 2939.
26. Chisholm, M. H.; Clark, H. C.; Manzer, L. E.; Stothers, J. B.; *J. Am. Chem. Soc.* **1972**, *94*, 5087.
27. Moseley, K.; Maitlis, P. M.; *J. Chem. Soc. Chem. Commun.* **1971**, 982.
28. Goodwin, H.A.; Lions, F.; *J. Am. Chem. Soc.* **1959**, *81*, 6415.
29. Ferraro, J. R.; *Low-Frequency Vibrations of Inorganic and Coordination Compounds*, Plenum Press: New York, 1971, ch. 8.
30. Kemp, W.; *NMR in Chemistry: A Multinuclear Introduction*; 1st ed., MacMillan: London, 1986, pp. 84-107.
31. Gay, I. D.; Young, G. B.; *Organometallics* **1996**, *15*, 2264, and references therein.

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