

Figure 3. The metal-based aryl-to-cyclohexadiene conversion in relation to aromatic electrophilic substitution.

tions involving organometallic species with η^5 or η^6 ring systems have been reported and in several instances have been shown to have synthetic utility.²⁰ Consequently, to help elucidate the operative mechanism(s), there is currently much interest in those cases where regio- or stereoselectivity is observed.²¹

In our system the nucleophilic additions to arenonium complex 1 (and its synthesis from cationic 2 and MeI) are unique examples of such reactions occurring on a C_6 ring

(20) Birch, A. J.; Jenkins, I. D. "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1976; Vol. I, Chapter I, pp 1-82. Jaouen, G. "Transition Metal Organometallics in Organic Synthesis"; Alper, H., Ed.; Academic Press: New York, 1978; Vol. II, Chapter II, pp 65-120.

(21) See, for example: Birch, A. J.; Stephenson, G. R. *J. Organomet. Chem.* 1981, 218, 91-104 and references therein.

system which has a σ -bonded metal substituent. In many respects the behavior shown has a direct counterpart in electrophilic substitution reactions of benzene rings, with each step stabilized by the Pt-I group (see Figure 3). Some stabilization of the nucleophilic addition products 3 and 4 may be additionally derived from release of ring strain inherent in the two five-membered chelate rings of 1 which contain the CH_2NMe_2 groups. However, much of the chemistry and particularly the stability of 1 can be understood in terms of the nature of the available leaving groups in the various products.

From the organic carbonium ion (Wheland intermediate) the proton, H^+ , is a good leaving group in the presence of a nucleophile. For complex 1 a subsequent step with a nucleophile cannot follow a "normal" electrophilic substitution sequence because both the introduced Me and the Pt-I units are bad leaving groups (due to the presence of a C-C σ bond and strong N-Pt-N coordination, respectively). Under special circumstances however, normal substitution takes place for example with CN^- (which possibly disrupts the Pt-N donor bonds) and those reactions with H_2O and aqueous NaX (that possibly rely on the intervention of hydroxide ion). Unfortunately in the latter instances we know nothing of the intermediates which provide the route to the C-C bond cleavage. Despite this gap in our knowledge the reaction of 1 with H_2O to afford 2 completes a metal center promoted reversible aryl to cyclohexadiene conversion illustrated in Figure 3). The key complex in the various high yield reaction steps is carbonium species 1, and further research is being concentrated on the potential of this complex, not only as a model but also as a route to substituted aryl compounds.

Acknowledgment. Professor K. Vrieze is thanked for his continuing interest in this work and his helpful discussions.

Registry No. 1, 82581-77-9; 2, 82112-93-4; 3a, 82581-78-0; 3b, 82581-79-1; 4a, 82581-80-4; 4b, 82581-81-5; 4c, 82581-82-6; $PC\equiv C^- Na^+$, 1004-22-4; $PC\equiv C^- Li^+$, 1122-79-8; OH^- , 14280-30-9; NaOMe, 124-41-4; $CH(CO_2Me)_2^- Na^+$, 18424-76-5; $CH(CO_2Me)_2^- K^+$, 61111-62-4; NaI, 7681-82-5; NaCN, 143-33-9; NaCl, 7647-14-5; NaBr, 7647-15-6; $[Pt\{C_6H_3(CH_2NMe_2)_{2-o,o}\}]$, 82112-97-8; $[PtCl\{C_6H_3-(CHNMe_2)_{2-o,o}\}]$, 82112-96-7; $[PtBr\{C_6H_3(CHNMe_2)_{2-o,o}\}]$, 67507-09-9; HBF₄, 16872-11-0.

Characterization of the Initially Precipitated Complexes from the Reaction of Zeise's Dimer and Hydrocarbons Containing a Cyclopropane Ring

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The initially precipitated complexes resulting from the reaction of Zeise's dimer with four compounds containing a cyclopropane ring have been characterized by MAS/CP NMR spectroscopy. For hydrocarbons 1, 3, and 9, the precipitate has the same *exo*-platinacyclobutane stereochemistry as the pyridine-solubilized complex. The ¹³C NMR resonances for the carbons which are σ bonded to the platinum show an upfield shift of 13-20 ppm on going from the initial precipitated to the pyridine-solubilized complex. In addition, the solid-state NMR spectra were also acquired for (norbornadiene)platinum dichloride (NBD-PtCl₂) and 2-phenylplatinacyclobutane.

Introduction

In nearly all of the examples reported to date, the reaction of Zeise's dimer with compounds containing a cyclopropane ring results in the formation of a yellow pre-

cipitate. Due to its relative insolubility most investigators have chosen to work with a solubilized form that is generated by reacting the precipitate with a coordinating solvent such as pyridine, THF, etc. Except for the work

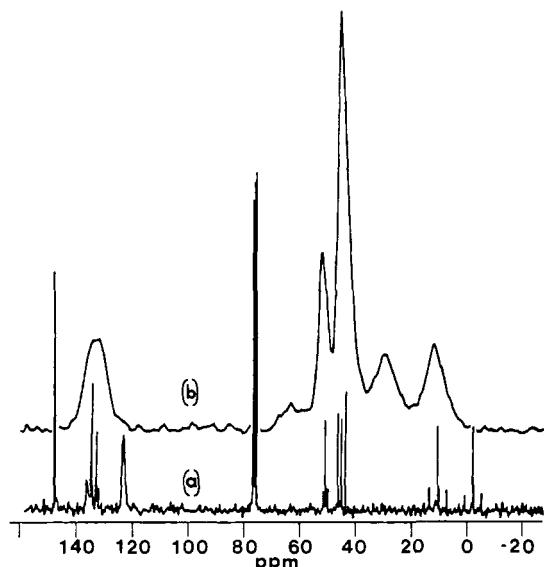
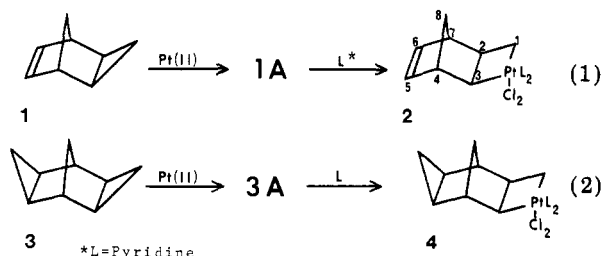


Figure 1. (a) The solution ^{13}C NMR spectrum of complex 2. (b) The MAS/CP NMR spectrum of complex 1A.

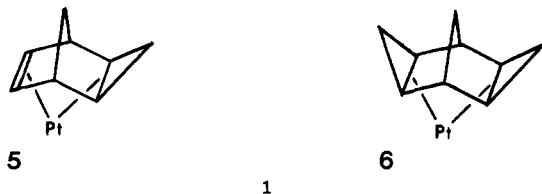
of Binns,¹ who through the use of mass spectrometry suggested that this precipitate is a tetrameric unit (structure 8), it has not been further characterized. This leaves open the question of the organic moiety which may or may not have the same structure in the initial precipitate as the solubilized complex. Therefore, we decided to investigate the characteristics of a few of these complexes by magic angle spinning/cross polarization (MAS/CP) NMR spectroscopy.

Results and Discussion

Recently, we reported² on two reactions (eq 1 and 2) in



which the initially precipitated complexes 1A and 3A were solubilized by reaction with pyridine. Volger³ had previously postulated structures 5 and 6 for these initial precipitates. However, since 5 and 6 differ from the reaction products 2 and 4, we felt that it would be prudent to make a more thorough investigation.



In the following discussion, comparisons between solution and solid-state ^{13}C NMR spectra will be presented for

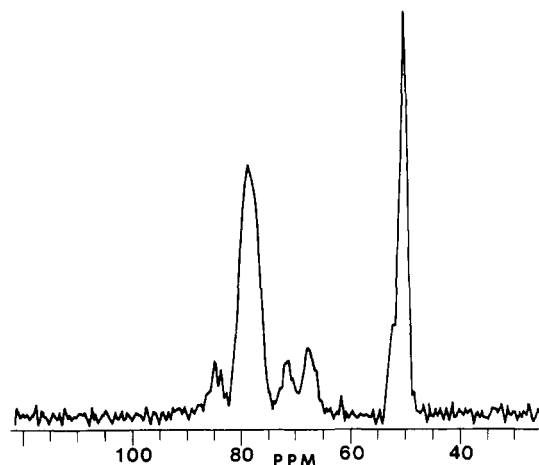


Figure 2. The ^{13}C MAS/CP NMR spectrum of NBD-PtCl₂.

the platinum complexes formed from hydrocarbon substrates 1, 3, and 9. The spectra for complexes from hydrocarbon 1 are shown in Figure 1. The outstanding NMR spectral feature² for *exo*-platinacyclobutane complexes such as 2 and 4 in solution is the upfield resonances which exhibit large coupling to ^{195}Pt (Figure 1). For compound 2 these resonances occur at 10.7 (C-3) and -2.2 ppm (C-1) with $J_{\text{Pt,C}} = 403$ and 371 Hz, respectively. It is also important to note that the olefinic resonances at 134.9 and 136.3 ppm, which are unfortunately partially obscured by the pyridine ligand resonances, do not have equivalent chemical shifts. The former is coupled to ^{195}Pt by 37 Hz.²

The magic angle spinning spectrum of 1A is a five-line spectrum with a broad olefinic resonance at 136 ppm and two broad upfield resonances at 32.5 and 15 ppm. The latter two are tentatively assigned to carbons which are bound to platinum by σ bonds and are discussed below. The fact that the olefinic carbon resonance occurs at virtually the same chemical shift in both spectra suggests that the olefin is not coordinated to the platinum as originally proposed by Volger.³ We propose that in fact the breadth of the 136 ppm resonance in the solid-state spectrum of 1 is due to two olefinic peaks.

Corroboration of the idea that the olefinic carbons are not coordinated to platinum rests further on the MAS/CP data collected for the complex (NBD)-PtCl₂ (Figure 2). In this complex the platinum moiety is situated endo with respect to the bicyclic ring and coordinated to both olefins.⁴ The olefinic resonance occurs at 78 ppm with a $J_{\text{Pt,C}}$ of 650 Hz (satellites at 72 and 85 ppm). The bridgehead carbons resonate at 50 ppm, and the bridge methylene carbon occurs at 67 ppm. The important point here is the fact that the olefinic resonance has shifted upfield 63 ppm on coordination to platinum, since the olefinic resonance for uncomplexed norbornadiene is at 141 ppm. Thus, the olefinic carbons in complex 1A must not be coordinated to the platinum.

Returning again to the discussion of the spectra in Figure 1, the resonance at 51.4 ppm which shows coupling to platinum and has been assigned to C-2 in the solution spectrum² has a counterpart in the upper spectrum at 54.5 ppm. Likewise the three resonances in the 46-ppm region appear to be mirrored in the large resonance at 47.5 ppm.

(4) Although the crystal structure of NBD-PtCl₂ has not been done, the analogous structure, NBD-PdCl₂, has been accomplished.^{5,6} Infrared studies by Wertz⁵ clearly shows that these are analogous structures. Furthermore, the NMR data presented herein accommodate the endo bidentate structure for NBD-PtCl₂.

(5) (a) Wertz, D. W.; Moseley, M. A. *Spectrochim. Acta, Part A* 1980, 36A, 467. (b) Baenzinger, N. C. *Acta Crystallogr.* 1961, 14, 303.

(1) Binns, S. E.; Cragg, R. H.; Gillard, R. D.; Heaton, B. T.; Pilbrow, M. F. *J. Chem. Soc. A* 1969, 1227.

(2) Waddington, M. D.; Jennings, P. W. *Organometallics* 1982, 1, 385.

(3) Volger, H. C.; Hogeveen, H.; Gaasbeek, M. M. P. *J. Am. Chem. Soc.* 1969, 91, 2137.

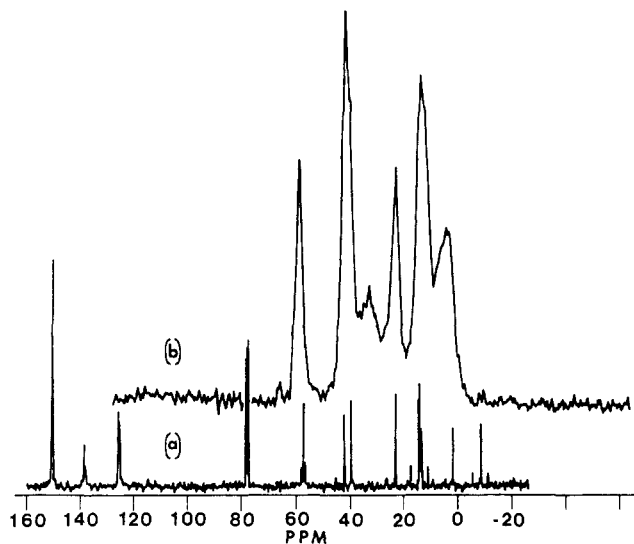
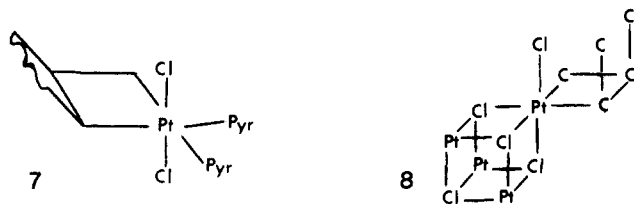


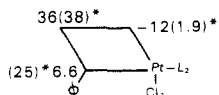
Figure 3. (a) The solution ^{13}C NMR spectrum of complex 4. (b) The ^{13}C MAS/CP NMR spectrum of complex 3A.

Thus, it appears that six of the eight resonances in the solution spectrum correspond to those in the solid-state spectrum. The remaining question is, what is the origin of the broad peaks at 32.5 and 15 ppm in the solid-state spectrum?

We are convinced that these resonances correspond to those at 10.7 and -2.2 ppm of the solution spectrum and that the chemical shift difference is a result of a ligand change in going from solid to solution complex. When pyridine is present, it should occupy the positions which are trans to each of the σ -bound carbon atoms of the platinumocyclobutane ring in the octahedral complex, structure 7.⁶ However, in complexes 1A or 3A, the oc-



tahedral structure is part of a tetrameric unit in which the positions trans to σ -bound carbon atoms are occupied by Cl atoms (partial structure 8).¹ Further evidence for this chemical shift change was obtained by investigating the products from phenylcyclopropane.⁷ For 2-phenylplatinacyclobutane, the resonances of the tetrameric precipitate and the pyridine adduct are shown in the structure below. Again the carbons directly attached to the platinum exhibit different chemical shift positions in going from the tetrameric to the solubilized complex.



*The numbers in parentheses equal the MAS/CP resonances.

(6) McQuillan, F. J.; Powell, K. G. *J. Chem. Soc., Dalton Trans.* 1972, 2123; *Tetrahedron Lett.* 1971, 3313.

(7) Both reviewers suggested that a simpler system such as cyclopropane would add clarity to this paper. Thus, since we had already begun some analyses of 2-phenylplatinacyclobutane, data for it is included. A mixture containing a 80:20 ratio of 2-phenyl to 3-phenyl was prepared by the method of Puddephatt⁸ and analyzed with MAS/CP.

(8) Al-Essa, R. J.; Puddephatt, R. J.; Quyser, M. A.; Tipper, D. F. H. *J. Am. Chem. Soc.* 1979, 101, 364.

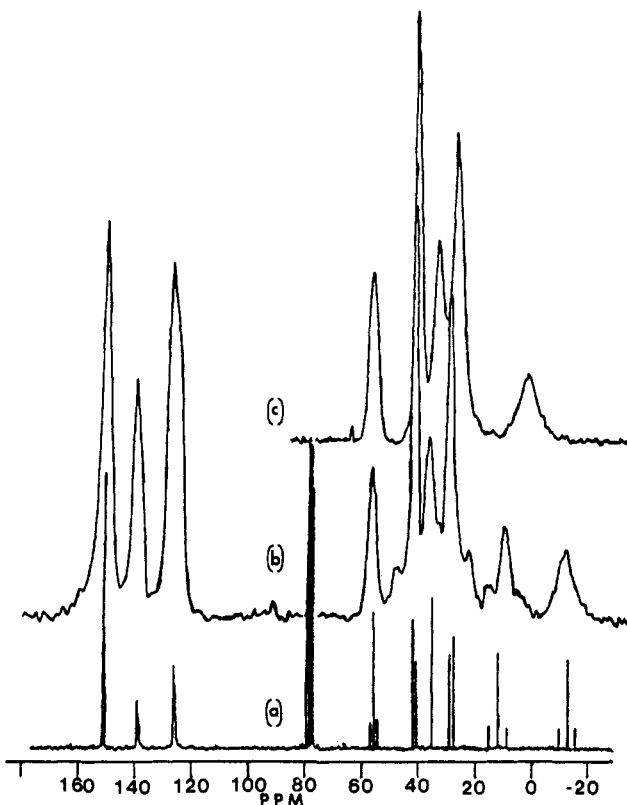
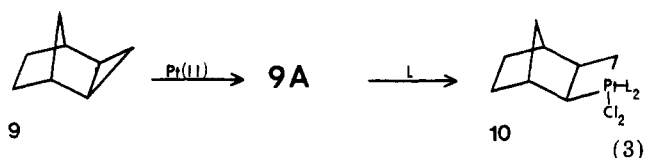


Figure 4. (a) The solution ^{13}C NMR spectrum of complex 10. (b) The ^{13}C MAS/CP NMR spectrum of complex 10. (c) The ^{13}C MAS/CP NMR spectrum of complex 9A.

In summary, we suggest that the structure for 1A is the same as that shown for the Pt(IV) complex 2 without the pyridine ligands and that there is no evidence for association of the platinum moiety with the olefin as proposed for structure 5.

The structure of 3A (eq 2) was also investigated in order to test the validity of structure 6. With use of the same logic as used above, the results (Figure 3) suggest that the structure of 3A is indeed a platinacyclobutane complex analogous to 4. In this example the resonances for the carbons bound to ^{195}Pt are at -9 and 13.8 ppm in the solution spectrum and at 4 and 33 ppm in the solid-state spectrum. Save these two resonances there is excellent agreement between the solution and solid-state spectra.

A third and final reaction was investigated (eq 3) because the reaction substrate could not form an endo bidentate structure analogous to 5 and 6. Thus, the results,



if successful, could be related to structures 1A, 3A, 2, and 4 and would thereby provide an additional and definitive statement on the validity of the above arguments. The results shown in Figure 4 not only provided the definitive statement but also provided data on possible chemical shift differences that might occur on changing phase. It is apparent in comparing the two lower spectra in Figure 4 that there is very little change in chemical shift positions relative to phase change. As in the previous examples, the upper most spectrum of 9A agrees very well with the two spectra below it save the resonances of the platinum bound carbons which have a resonance at 4 and presumably around 33 ppm. Thus, it is reasonable to again conclude

that the organic moiety of **9A** is basically the same as that for structure **10**.

Conclusion

Results of comparing solution and solid-state NMR spectra suggest that the initial precipitated platinum complexes from Zeise's dimer and hydrocarbons **1**, **3**, and **9** are platinumacyclobutane complexes. These results are in contrast to previous data which had suggested that two of these compounds were endo bidentate complexes. Moreover, the solid-state spectrum of **10** is in excellent agreement with its solution spectrum showing that the phase does not have a significant perturbation on the chemical shift. There are precautionary notes to be made here. We have been careful to speak of these precipitates as initial precipitates. It would be erroneous to *always* consider these as the initially formed complex. Further, it is likely to be erroneous to assume that the initial precipitate and the solubilized complex are always the same. However, MAS/CP NMR spectroscopy has been shown to be a viable tool in investigating this aspect of organometallic chemistry.

Experimental Section

General Data. ^1H , ^{13}C , and ^{196}Pt NMR spectra were obtained by using a Bruker WM-250 spectrometer. MAS/CP spectra were obtained at 37.7 or 50.2 MHz for ^{13}C . Diethyl ether was distilled from CaH_2 prior to use. Pyridine was Baker reagent grade, and CDCl_3 was obtained from Stohler. Zeise's dimer was prepared from K_2PtCl_4 which was purchased from Aldrich. The hydrocarbons **1** and **3** as well as their initially precipitated platinum complexes were prepared as previously described.² Analyses were done by Galbraith Laboratories and were correct for all complexes.

Preparation of 9. *exo*-Tricyclo[3.2.1.0^{2,4}]octane was prepared by the method of Kottwitz⁹ and purified by gas chromatography.

Preparation of 9A. To a suspension of 506 mg (0.86 mmol) $[\text{C}_2\text{H}_4\text{PtCl}_2]_2$ in 10 mL of dry ether was added 360 mg (3.3 mmol) of **9**. This mixture was magnetically stirred at reflux for 5 h during which time the orange solid, Zeise's dimer, was consumed, giving the yellow solid of the platinum complex. This product was filtered and dried by vacuum. Subsequently, it was resuspended in ether by crushing and stirring. Filtration and drying in a vacuum desiccator gave 610 mg of a yellow solid—yield 95%. Shorter reaction times afforded a lower conversion to product.

Preparation of 10. To **9A** (200–600 mg) suspended in 10–15 mL of chloroform was added 3–4 equiv of pyridine with magnetic stirring. After 5 min, the yellow solid dissolved and the volatile components were removed by rotoevaporation at 25 °C to yield a dark yellow oil. Addition of pentane and further rotoevaporation afforded a yellow-white solid. Trituration in more pentane, solvent evaporation, and vacuum desiccation gave the yellow-white pyridine complex in quantitative yield.

Solution Spectra of Pyridine Adducts. Solution spectra for the pyridine derivatives of **2**, **4**, and **10** were obtained by adding 3–4 equiv of pyridine to stirred suspensions of platinum compound in CDCl_3 . Rotoevaporation of these solutions and workup as described for structure **10** yielded solid pyridine derivatives for each of the compounds.

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Registry No. **1**, 3635-94-7; **1A**, 82839-00-7; **2**, 82839-01-8; **3**, 24506-61-4; **3A**, 82839-02-9; **4**, 82839-03-0; **9**, 13377-46-3; **9A**, 82839-04-1; **10**, 82839-05-2; $[(\text{C}_2\text{H}_4)\text{Cl}_2\text{Pt}]_2$, 12073-36-8.

(9) Kottwitz, J.; Vorbruggen, H. *Synthesis* 1975, 636.

Highly Reduced Organometallics. 8.¹ The Synthesis of (Phosphine)pentacarbonylvandate(1–) Anions, $\text{V}(\text{CO})_5\text{PR}_3^-$, by the Thermal Substitution of (Ammine)pentacarbonylvandate(1–), $\text{V}(\text{CO})_5\text{NH}_3^-$

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(Ammine)pentacarbonylvandate(1–) reacts with various phosphines ($\text{L} = \text{Ph}_3\text{P}$, $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 0-2$), $(p\text{-ClC}_6\text{H}_4)_3\text{P}$, Me_3P , HPh_2P , F_3P) to provide moderate to high yields of $\text{V}(\text{CO})_5\text{L}^-$. Several of these materials have not been isolated previously and either are unavailable or are not easily prepared by other methods. Interestingly, the reaction of $\text{V}(\text{CO})_5\text{NH}_3^-$ with Ph_4P_2 in liquid ammonia provides high yields (70–75%) of previously unknown $\text{V}(\text{CO})_5\text{Ph}_2\text{PNH}_2^-$, isolated as the Et_4N^+ salt, while the same reaction conducted in THF provides lower yields (35–45%) of $\text{V}(\text{CO})_5\text{Ph}_4\text{P}_2^-$, isolated as the Ph_4P^+ and Ph_4As^+ salts. Proton-decoupled ^{31}P NMR has been used to unambiguously show that $\text{V}(\text{CO})_5\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2^-$ ($n = 0-2$) contain both ligated and unligated diphenylphosphino groups. Infrared and ^1H NMR spectra of the products are also discussed with respect to proposed structures. This "labile ligand method" represents the best method presently available for the synthesis of $\text{V}(\text{CO})_5\text{PR}_3^-$ species.

Introduction

Phosphine-substituted carbonyl anions of vanadium are known to be generally much more reactive than $\text{V}(\text{CO})_6^{-2,3}$

and are potentially useful precursors to new transition-metal clusters containing vanadium, which are presently very uncommon species.⁴ The first reports of a phosphine-substituted carbonylvandate anion appeared in

(1) Part 7: Ellis, J. E.; Fjare, K. L. *Organometallics* 1982, 1, 898.

(2) Ellis, J. E.; Faltynek, R. A. *J. Organomet. Chem.* 1975, 93, 205.

(3) Davison, A.; Ellis, J. E. *J. Organomet. Chem.* 1972, 36, 113.

(4) Ellis, J. E. *J. Am. Chem. Soc.* 1981, 103, 6106.