the stereochemistry of the phenol oxidation reactions are in progress.

References and Notes

(1) (a) D. H. R. Barton and T. Cohen, "Festschrift A. Stoll", Birkhäuser, Basel, 1957, p 117; (b) W. I. Taylor and A. R. Battersby, Ed., "Oxidative Coupling of Phenols", Marcel Dekker, New York, N.Y., 1967; (c) A. I. Scott, *Q. Rev., Chem. Soc.*, **19,** 1 (1965); (d) D. H. R. Barton, Pedlar Lecture, *Chem. Brit.*, **3,** 330 (1967); (e) T. Kametani and K. Fukumoto, *Synthesis*, 657 (1972); (f) S. M. Kupchan and A. J. Liepa, *J. Am. Chem. Soc.*, **95,** 4062 (1973); (g) T. Kametani, K. Fukumoto, and F. Satoh, *Bioorg. Chem.*, **3,** 430 (1974); (h) K. S. Brown, *Chem. Soc. Rev.*, **4,** 263 (1975); (i) S. Tobinaga, *Bioorg. Chem.*, **4,** 110 (1975).

(2) (a) H. Musso, *Angew. Chem.*, **75,** 965 (1963); (b) P. D. McDonald and G. A. Hamilton, in "Oxidation in Organic Chemistry", Part B, W. S. Trahanovsky, Ed., Academic Press, New York, N.Y., 1973, Chapter 2; (c) M. A. Schwartz, R. A. Holton, and S. W. Scott, *J. Am. Chem. Soc.*, **91,** 2800 (1969); (d) M. A. Schwartz, B. F. Rose, and B. Vishnuvajjala, *ibid.*, **95,** 612 (1973).

(3) B. R. Brown in ref 1b.

(4) To our knowledge Bobbitt's electrochemical oxidation of a tetrahydroisoquinoline is the first and only example of an investigation into the stereospecificity of the phenol coupling reaction. J. M. Bobbitt, J. Noguchi, H. Yagi, and K. H. Weisgraber, *J. Am. Chem. Soc.*, **93,** 3551 (1971).

(5) Optically active phenol (*S*)-(+)-I was prepared by standard methods from optically active 1-carboxy-5,6-dimethyl-7-hydroxy-1,2,3,4-tetrahydronaphthalene ((*S*)-(−)-III). The latter compound was resolved through its 1-(+)-dehydroabietylamine salts and the optical purity of (*S*)-(+)-I, determined by examination of the 100-MHz ^1H NMR spectrum of the 1-(−)-α-phenylethylamide of III was > 97.5%. The configurations of (*S*)-(−)-III and (*S*)-(+)-I were independently correlated using the ORD and CD Cotton effects, with the unsubstituted 1-methyl- and 1-carboxytetralins of known absolute configurations;[5a] substituent influences were determined by helicity- and sectorrules for the ^1L_b transition.[5b] (a) J. Barry, H. B. Kagan, and G. Snatzke, *Tetrahedron*, **27,** 4737 (1971); B. Sjoberg, *Acta Chem. Scand.*, **14,** 273 (1960); (b) G. Snatzke, M. Kajtar, F. Snatzke in "Fundamental Aspects and Recent Developments in Optical Rotatory Dispersion and Circular Dichroism", F. Ciardelli and P. Salvadori, Ed., Heyden & Sons, London, New York, Theime, 1973, Chapter 3.4.

(6) All new compounds gave satisfactory elemental analysis and spectral data in agreement with the structure.

(7) The entire crude dimer fraction, without purification, was examined minutely using 100-MHz ^1H NMR, TLC, and HPLC. Only dimer II_a was found to be present. No trace of dimer II_b could be detected. Since we had been able to detect this dimer II_b in 8% quantities in the more complex mixture, we feel certain about its absence in this case.

(8) K. Mislow, *Top. Stereochem.*, **4,** 1–42 (1968).

(9) S. F. Mason, R. H. Seal, and D. R. Roberts, *Tetrahedron*, **30,** 1671 (1974)

(10) W. Hug and G. Wagniere, *Tetrahedron*, **28,** 1241 (1972).

(11) J. P. Ferris et al., *J. Am. Chem. Soc.*, **93,** 2963 (1971).

(12) (a) Both reactions (coupling of (*S*)-(+)-I and of (*RS*)-I) were run under identical conditions including a completely quantitative (nonfractionating) workup. The entire dimer fraction, isolated via preparative TLC, was first subjected to a careful NMR analysis prior to further purification. This fraction showed a correct total elemental analysis. The 100-MHz ^1H NMR spectrum uniquely identifies the three *dl*-pairs. In addition complete separation was achieved via HPLC (Waters Liquid Chromatograph, column 50 cm × ⅜, Si 60-5, Prop. Cl, hexane 1:1) and *all* three diastereomeric dimers were individually identified (exact mass determination). All other spectral data of the individual diastereomers were obtained.

(13) We will not at this time try to speculate whether or not such a complex incorporates part of the $K_3Fe(CN)_6$ moiety.

(14) See, for example, the elegant work by S. Shibata and co-workers on the Ustilaginoidins. S. Shibata, *Chem. Brit.*, **3,** 110 (1967).

(15) We thank the Netherlands Organization for Pure Research (ZWO) for a graduate fellowship.

Ben Feringa,[15] Hans Wynberg*
Department of Organic Chemistry
The University, Zernikelaan
Groningen, The Netherlands

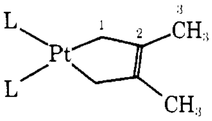
Received September 22, 1975

Organoplatinum Complexes Related to the Cyclodimerization of 1,3-Dienes. Reactions of 2,3-Dimethylbuta-1,3-diene and Buta-1,3-diene with Bis(cycloocta-1,5-diene)platinum or Bis(ethylene)trimethylphosphineplatinum

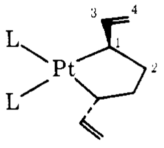
Sir:

The discovery and development of the nickel(0) catalyzed cyclodimerization and cyclotrimerization reactions of 1,3-dienes rank as one of the major achievements of organometallic chemistry.[1] Considerable progress has been made towards understanding the mechanisms of these reactions; however, there are certain aspects which still require clarification. The recent development of syntheses[2] of "ligand free"[3] zerovalent compounds of platinum now allows a study of reactions of these species with 1,3-dienes. Herein we report studies with bis(cycloocta-1,5-diene)platinum.[4]

Reaction (room temperature, 1 h) of an excess of 2,3-dimethylbuta-1,3-diene with bis(cycloocta-1,5-diene)platinum afforded (84% yield) the white crystalline complex I,[5] mp 95° dec [^{13}C NMR resonances (C_6D_6, ^1H decoupled, measured downfield from Me_4Si) at 20.1 ppm, C(3) ($J_{PtC(3)} = 111.4$ Hz); 40.7, C(1) ($J_{PtC(1)} = 787.4$ Hz); and 136.4, C(2) ($J_{PtC(2)} = 0$Hz); resonances due to coordinated C_8H_{12} occur at 29.6 and 96.8 ppm ($J_{PtC} = 51.9$ Hz)]. Treatment of I with *tert*-butylisocyanide led to the displacement of cycloocta-1,5-diene and the formation of II, mp 84–86° [^{13}C NMR resonances (C_6D_6, ^1H decoupled) at 21.4 ppm, C(3) ($J_{PtC(3)} = 96.1$ Hz); 30.9, C(1) ($J_{PtC(1)} = 608.8$ Hz); and 136.2, C(2) ($J_{PtC(2)} = 46.2$ Hz); together with resonances due to coordinated *t*-BuNC]. Thus, the reaction involves an oxidative 1,4-addition of a Pt(0) species to the 1,3-diene to form a platinacyclopent-3-ene. Although this mode of metal–diene interaction has been observed previously with Ni(0) complexes[6] and the perfluorinated diene CF_2:CFCF:CF_2, this is the first example of such a reaction with a hydrocarbon.[7]



(I, L_2 = 1,5-C_8H_{12})
(II, L = *t*-BuNC)



(III, L_2 = 1,5-C_8H_{12})
(IV, L = *t*-BuNC)

It is likely that the reaction involves the intermediacy of (cycloocta-1,5-diene)(2,3-dimethylbuta-1,3-diene)platinum(0), which undergoes an electronic rearrangement to form the Pt(II) five-membered ring species. There has been considerable discussion about the possibility that bisolefin complexes could reversibly transform into a metallocyclopentane.[8]

In contrast, buta-1,3-diene reacts (room temperature, 2 h) with $[Pt(1,5\text{-}C_8H_{12})_2]$ to form complex III, mp 110 °C. Examination of the ^1H and ^{13}C NMR spectra showed that III was a 2,5-divinylplatinacyclopentane; however, the important question as to the relative configuration of the vinyl groups remained undefined. A single-crystal x-ray diffraction study established the structure shown in Figure 1. Crystal data: $C_{16}H_{24}Pt$; monoclinic; $P2_1/n$; $Z = 4$ in a unit cell of dimensions $a = 9.082$ (6), $b = 10.554$ (13), $c = 15.293$ (4) Å; $\beta = 92.13$ $(7)^0$; R is currently 0.12 for 1487 reflections with $I \geqslant 2.0\sigma(I)$ (Syntex $P2_1$ four-circle diffractometer using Mo K_α radiation). The crystal of III was twinned and the resulting structure showed disorder; therefore, further structural confirmation was sought. Cycloocta-1,5-diene was displaced from III by *tert*-butyl isocyanide to give complex IV, mp 111–112°, whose crystal structure was also determined (Figure 2). Crystal data: $C_{18}H_{30}N_2Pt$; monoclinic; $P2_1/n$; $Z = 4$ in a unit cell of dimensions, $a = 9.317$ (4), $b = 12.284$ (12), $c = 19.217$ (15) Å; $\beta = 99.16(5)^0$; R is currently 0.10 for 1100 reflections with $I \geqslant 2.0\sigma(I)$.

Despite the problems of crystal imperfection the structures of both III and IV showed unequivocally that the vinyl groups lie on opposite sides of the five-membered ring with deviations of 0.84 and −0.97 Å in III and −0.64 and 0.71 Å in IV, respectively, from the mean coordination plane. An insight into the mode of formation of the *trans*-2,5-divinylplatinacyclopentane ring system was obtained from a study of the reaction of bis(ethylene)trimethylphosphineplatinum with buta-1,3-

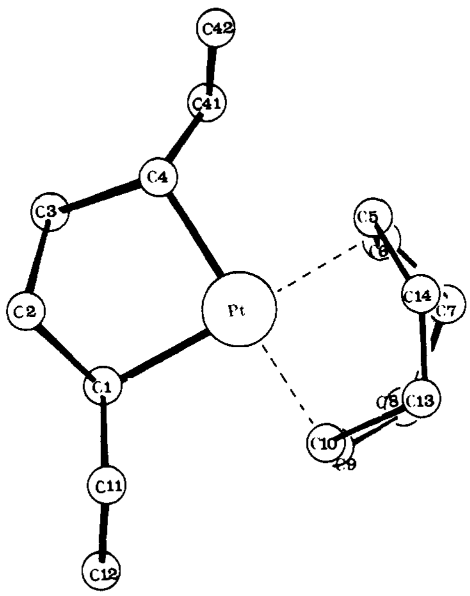


Figure 1. A view of the molecular structure of one of the independent molecules of [$\overline{\text{Pt}\cdot\text{CH(CH:CH}_2\text{)CH}_2\text{CH}_2\text{C}}$H(CH:CH$_2$)(C$_8H_{12}$)] showing the atomic numbering scheme, and projected onto the mean plane of C1, C4, Pt, C5,6, and C9,10: Pt–C(olefin), 2.32 (6); Pt–C(σ), 2.21 (5) Å; ∠C1PtC4, 85°.

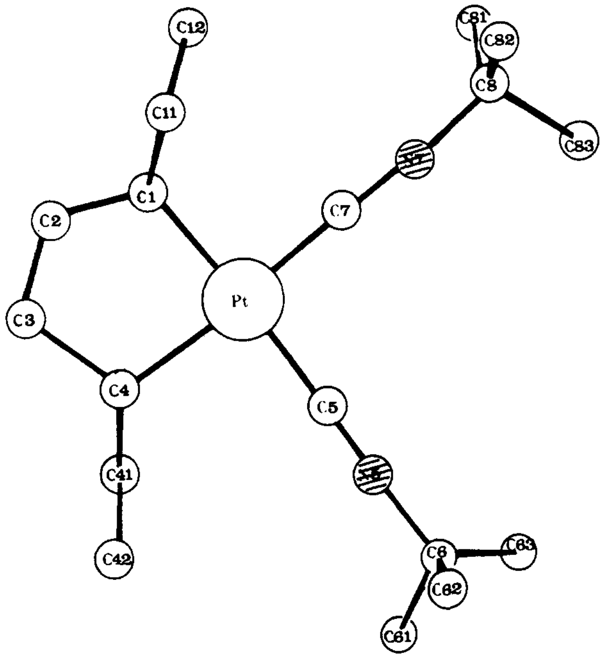
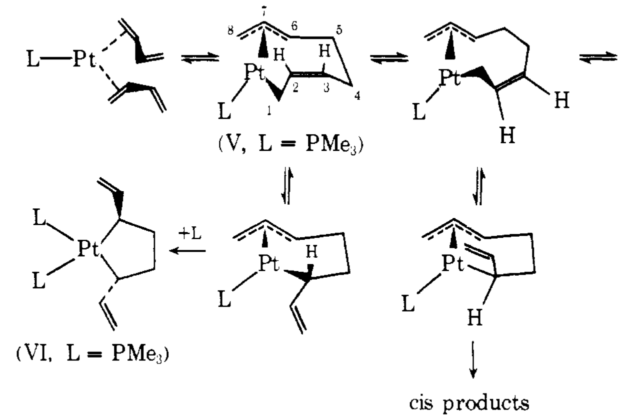


Figure 2. A view of the molecular structure of one of the independent molecules of [$\overline{\text{Pt}\cdot\text{CH(CH:CH}_2\text{)CH}_2\text{CH}_2\text{C}}$H(CH:CH$_2$)($t$-BuNC)$_2$] showing the atomic numbering scheme, and projected onto the mean plane of C1, C4, Pt, C5, C7: Pt–C(σ), 2.07 (4); Pt–C(t-BuNC), 1.84 (4) Å; ∠C1PtC4, 82°.

diene. Similar results were obtained with the analogous tricyclohexylphosphine, triphenylphosphine, or triethylphosphine complexes. The white crystalline product V, mp 90–93° dec, showed a very similar ^{1}H NMR spectrum to that reported[9] for 1-η^1-6,7,8-η^3-*cis*-2-*trans*-6-octadienediyl(tricyclohexylphosphine)nickel and the illustrated structure was further confirmed by a ^{13}C NMR spectrum [C_6D_6, ^{1}H decoupled: 4.4 ppm C(1) ($J_{PtC(1)} = 640.4$, $J_{PC(1)} = 4.9$ Hz); 17.1, (PMe$_3$); 25.2, C(4) and C(5); 49.9, C(8) ($J_{PtC(8)} = 55.7$ Hz); 64.4, C(6) ($J_{PtC(6)} = 44.0$, $J_{PC(6)} = 36.1$ Hz); 108.7, C(7) ($J_{PtC(7)} = 32.3$, $J_{PC(7)} = 2.0$ Hz); 112.6, C(3) ($J_{PtC(3)} = 59.6$ Hz); and 134.2, C(2) ($J_{PtC(2)} = 78.1$, $J_{PC(2)} = 2.0$ Hz)] and by a single-crystal x-ray diffraction study (−60°). Crystal data: $C_{11}H_{21}PPt$; orthorhombic; *Pnam*; $Z = 4$ in a unit cell of dimensions $a = 15.979$ (15), $b = 9.017$ (24), $c = 8.992$ (7) Å; R is currently 0.064 for 1291 reflections with $I \geqslant 2.0\sigma(I)$; Pt–C(8) = 2.18 (3), Pt–C(7) = 2.11 (3), Pt–C(6) = 2.15 (3), Pt–C(1) = 2.15 (3), Pt–P = 2.229 (6) Å. The structure showed disorder about a crystallographic mirror plane; the atoms C(7) and C(1) occupying two sites with equal probability.

Scheme I



Reaction (room temperature, 1 h) of V with 1 molar equiv of trimethylphosphine affords complex VI, mp 92–94° dec, the bis(trimethylphosphine) analogue of III and IV. In addition, treatment of III with 1 mol of trimethylphosphine yields V. The formation of III, IV, and VI with a trans-divinyl stereochemistry is somewhat unexpected in view of the suggestion[1] that a *cis*-divinylnickelacyclopentane is the precursor of *cis*-divinylcyclobutane in the Ni(0) catalyzed dimerization of buta-1,3-diene. We believe that this suggestion is essentially correct, but that we must also take into account the different conformations which the π-allyl-C_8 chain can adopt. This is illustrated in Scheme I.[10] In the case of platinum the conformation leading to the trans-divinyl stereochemistry is preferred.

Acknowledgments. We thank the Science Research Council for support (Grants B/RG/2768 and 88577).

References and Notes

(1) For a complete survey see P. W. Jolly and G. Wilke, "The Organic Chemistry of Nickel", Vol. II, "Organic Synthesis", Academic Press, New York, N.Y., 1975.
(2) M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 3, 449 (1975); *J. Chem. Soc., Dalton Trans.,* in press.
(3) Defined in ref 1, p 134, as a system in which the only ligands associated with the metal are organic groups readily displaced by the reactant.
(4) First reported by J. Muller and P. Goser, *Angew. Chem., Int. Ed. Engl.*, **6,** 364 (1967), but see ref 2.
(5) Satisfactory elemental analyses, mass spectra, and ^{1}H NMR spectra were obtained for all compounds described herein.
(6) J. Browning, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 453 (1971); M. Green, S. K. Shakshooki, and F. G. A. Stone, *ibid.*, 2828 (1971).
(7) Unsaturated fluorocarbons can serve as useful model substrates for their hydrocarbon analogues in reactions with d^{10} metal complexes, particularly in relation to formation of metallocycles. For a review see F. G. A. Stone, *Pure Appl. Chem.*, **30,** 551 (1972).
(8) R. H. Grubbs and T. K. Brunck, *J. Am. Chem. Soc.*, **94,** 2538 (1972); A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White, and J. A. Osborn, *J. Am. Chem. Soc.*, **95,** 597 (1973), and references cited therein.
(9) J. M. Brown, B. T. Golding, and M. J. Smith, *Chem. Commun.*, 1240 (1971).
(10) We assume that the precursor of V is a trigonal planar Pt(0) complex containing *cis*- and *trans*-buta-1,3-diene molecules bonded in the 1,2-η mode. A similar geometry is suggested by Heimbach and co-workers (ref 11) for the corresponding intermediate in the Ni(0) catalyzed reaction; however, Jolly and Wilke (ref 1) do not discuss this important question.
(11) H. Buchholz, P. Heimbach, H. J. Hey, H. Selbeck, and W. Wiese, *Coord. Chem. Rev.*, **8,** 129 (1972).

Geoffrey K. Barker, Michael Green, Judith A. K. Howard
John L. Spencer, F. Gordon A. Stone*
Department of Inorganic Chemistry, The University of Bristol
Bristol BS8 1TS, England

Received February 4, 1976