has a formal oxidation state of +6. Such oxidizing power as these molecules show comes from iodine. Under vacuum the tetraiodide gives off I_2 vapor to form the diiodide. Dissolving these compounds in olefins and then evaporating also yields the diiodides. Therefore, the formation of dialkyltellurium tetraiodides apparently involves direct incorporation of I_2 molecules, rather than showing iodine–iodine bond cleavage. Dialkyl sulfides and selenides form charge-transfer adducts with iodine,[7,9] while dialkyl tellurides are oxidized to R_2TeI_2.[11] Both α and β forms of $(CH_3)_2TeI_2$ show very extensive Te–I intermolecular interaction in the solid state.[12,13]

In principle, the I_2 molecules could bond to either the Te atom or to an I atom. Infrared and mass spectral studies, however, show no evidence for any triiodide groups in the solid state. Also, the almost negligible change in the Te–I stretching bands going from Me_2TeI_2 to Me_2TeI_4 suggests that the I_2 does not interact to any appreciable extent with the iodine atoms bonded to tellurium. Therefore, the dialkyltellurium tetraiodides most probably are solid-state adducts, perhaps with the distorted octahedral arrangement found for α-Me_2TeI_2 by Chan and Einstein.[12] Such a structure is consistent with the ready dissociation of tetraiodides and also with the observed instability of $(C_4H_9)_2TeI_4$ at room temperature.[3] We could not synthesize either $(C_5H_{11})_2TeI_4$ or $(C_6H_5)_2TeI_4$. The increasing size of the groups would enhance steric effects, hindering I_2 from approaching the tellurium and thereby lowering the stability relative to the diiodide.

Attempts to prepare $(CH_3)_2TeI_2Br_2$ from either the diiodide or the dibromide proved unsuccessful, probably because of the greater electronegativity and reduced size of bromine.

Experimental Section

Both di- and tetraiodides were prepared by methods elsewhere described.[3] Attempted synthesis of $(C_6H_5)_2TeI_4$ or $(CH_3)_2TeI_2Br_2$ by direct combination gave only unreacted starting materials.

Nuclear magnetic resonance spectra were run on a Varian T-60 recording spectrometer, using carbon tetrachloride as solvent and internal tetramethylsilane as standard. Ultraviolet and visible spectra were run on a Cary Model 14 recording spectrophotometer, using 1-cm quartz cells. Peak positions were determined to within ±1 nm. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-7 mass spectrometer, using an ionizing voltage of 70 eV and a pressure of 2×10^{-6} Torr. Far-infared spectra for the solid compounds were run on a Perkin-Elmer Hitachi FIS 3 spectrophotometer, while the spectra above 400 cm^{-1} were obtained on a Perkin-Elmer Model 337 recording spectrometer. Peak positions were determined to ±2 cm^{-1}.

Acknowledgments. This work was supported by a Frederick Gardner Cottrell grant from the Research Corp. We are grateful to Professor Kazuo Nakamoto of Marquette University for determining the far-infrared spectra. Mass spectra were run by Mr. Timothy Becker, and nmr spectra by Dr. A. J. Andy. The mass spectrometer was purchased through a National Science Foundation grant.

Registry No. $(CH_3)_2TeI_2$, 18879-38-4; $(CH_3)_2TeI_4$, 52585-06-5; $(C_2H_5)_2TeI_2$, 41235-19-2; $(C_2H_5)_2TeI_4$, 52645-35-9; $(C_3H_7)_2TeI_2$, 41235-20-5; $(C_3H_7)_2TeI_4$, 52645-36-0; $(C_4H_9)_2TeI_2$, 41235-21-6; $(C_4H_9)_2TeI_4$, 52730-57-1.

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Reactions of Dimethyl[diphenyl(*o*-vinylphenyl)phosphine]platinum(II), $Pt(CH_3)_2(SP)$, with Iodine and Iodomethane

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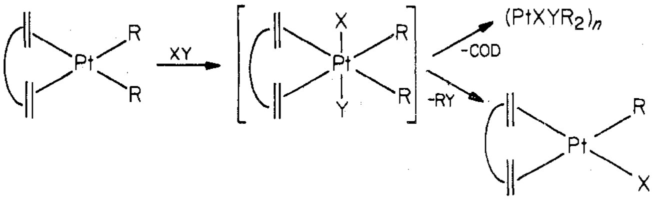
Stable olefin complexes of platinum(IV) are unknown, even for chelating diolefins such as 1,5-cyclooctadiene (COD).[1] Oxidative addition reactions by XY on complexes $PtR_2(COD)$ lead either to polymeric organoplatinum(IV) species, $(PtR_2XY)_n$ not containing COD, or to platinum(II) complexes PtRX(COD), presumably *via* a reactive platinum(IV) intermediate.[1] See Scheme I.

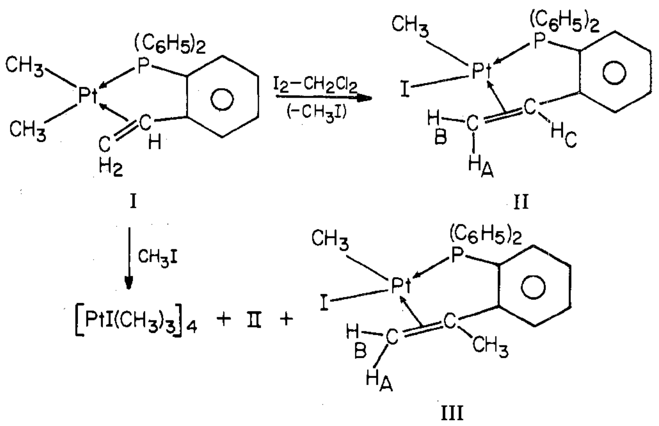
Scheme I



The reaction of $Pt(CH_3)_2(SP)$ (I), where SP = diphenyl(*o*-vinylphenyl)phosphine (*o*-styryldiphenylphosphine), with oxidative-addition reagents promised to be of interest since any platinum(IV)–olefin complex initially formed would be expected to be highly reactive.

The reaction of I with iodine in dichloromethane immediately gave a bright orange solution, suggesting formation of a platinum(IV) species, but the only compound which could be isolated or detected by ^1H nmr was pale yellow $PtI(CH_3)(SP)$ (II), identical in properties with a sample prepared by metathesis from $PtCl(CH_3)(SP)$. Compound II can arise by reductive elimination of iodomethane from a transient intermediate platinum(IV) complex, IVa, which may be monomeric as shown or dimeric with iodide bridges and an uncoordinated vinyl group.

Scheme II



An excess of iodomethane was added to $Pt(CH_3)_2(SP)$ (I) in dichloromethane; the solution was allowed to stand for 2 days and then was evaporated to dryness under reduced

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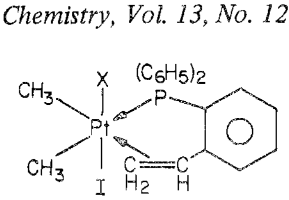
[1] H. C. Clark and L. E. Manzer, *J. Organometal. Chem.*, 59, 411 (1973).



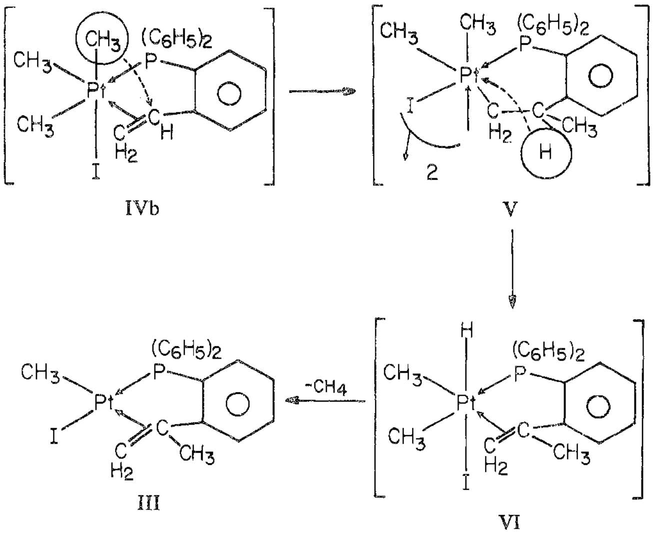
IVa, X = I
b, X = CH_3

pressure. The product showed a very complex pattern in its ^{1}H nmr spectrum in the region δ 0–2.5 ppm indicating the presence of a complex mixture of compounds. When this mixture was dissolved in chloroform and allowed to stand for several days, a new singlet peak appeared at δ 2.56 ppm with "satellites" from coupling to ^{195}Pt ($I = {}^1/_2$, 33.7% abundant, $J_{\text{Pt-H}} = 15.5$ Hz). The region upfield of this peak also became simpler, evidently corresponding to a mixture of a small number of complexes containing platinum methyl groups. When the reaction was carried out in an nmr tube, a peak corresponding to methane (δ 0.17 ppm) was observed.

Chromatography on Florisil using *n*-pentane–dichloromethane mixtures gave first trimethylplatinum iodide tetramer, $\{PtI(CH_3)_3\}_4$, identified by its characteristic nmr spectrum,[2] then a partially separated mixture of $PtI(CH_3)$(SP) (II), and a third product, which was responsible for the characteristic peak at δ 2.56. Fractional crystallization on samples rich in this product eventually gave a product sufficiently pure (~90%) to be adequately characterized, although it could not be completely freed from II. The ^{1}H nmr spectrum unambiguously showed the third product to be iodomethyl[(*o*-α-methylvinyl)phenyldiphenylphosphine]platinum(II), III. Thus, peaks at δ 3.95 and 5.8 ppm (with "satellites") clearly correspond to vinylic protons in an olefinic group bound to platinum, and the lack of observable coupling between them indicates that they must be geminal. By integration, the peak at δ 2.56 ppm (with "satellites") corresponds to three protons (*i.e.*, a methyl group). The *Pt*-CH_3 patterns in the ^{1}H nmr spectrum and the ^{31}P nmr spectrum are very similar to those in $PtI(CH_3)$(SP) (II) (see Experimental Section). These products may be explained in terms of initial oxidative addition to give an unstable platinum(IV) complex IVb (which, like IVa, may be monomeric or dimeric with iodide bridges and uncoordinated vinyl groups), which then decomposes by three alternative routes to the observed products, *i.e.*, with loss of SP to give $[PtI(CH_3)_3]_4$, with loss of ethane to give $PtI(CH_3)$(SP) (II), and with loss of methane to give III.

The formation of the first two products in this reaction is clearly analogous to processes occurring in the reactions of PtR_2(COD),[1] although the cleavage of the Pt–P bond on oxidation has no precedent. The product III is clearly not formed by direct attack of iodomethane on the coordinated olefin in I, since under typical conditions it is only produced after all iodomethane has been removed from the system. A plausible route to III (Scheme III) could involve migration of a methyl group from an initially formed oxidative addition product IVb to the double bond to form a chelate metal–carbon σ-bonded complex V. This could then eliminate methane, possibly *via* a hydrido complex VI. However, the detailed mechanism may well be more complex than suggested by this scheme and, in view of recent observations on insertions[3] and oxidative additions,[4,5] could well involve free-radical intermediates.

Scheme III



The vinyl group in SP has been shown to insert into Pt–H,[6] Mn–H,[7] and Mn–$COCH_3$[8] bonds, but it is unreactive toward the Pt^{II}–CH_3 bonds in $Pt(CH_3)_2$(SP) (I), $PtI(CH_3)$(SP) (II), and $[Pt(CH_3)(\text{acetone})(SP)]^+$,[9] all of which are indefinitely stable in solution. Pt^{II}–CH_3 bonds are normally only reactive to insertion by olefins with electron-withdrawing substituents, such as C_2F_4,[10] and no insertions involving Pt^{IV}–CH_3 bonds have been described.

An interesting feature of our reaction is the preferential transfer of the methyl group to the internal rather than to the terminal carbon atom of the vinyl group. The transfer of aryl or carboalkoxy groups from palladium(II) to olefins occurs predominantly, though not exclusively, at the terminal carbon atom.[11] External nucleophilic attack on coordinated olefinic ligands containing a vinyl group to give chelate metal–carbon σ-bonded species can occur either at the terminal or the internal carbon atom; *e.g.*, methanolysis of $PtCl_2SP$ involves attack at the terminal carbon atom,[12] whereas nucleophiles attack 2-vinylpyridine[13] and $(C_6H_5)_2P(CH_2)_nCH{=}CH_2$ (n = 1–3)[14,15] coordinated to platinum(II) predominantly at the internal (β) carbon atom. At least one case is known of a facile interchange between five- and six-membered chelate rings containing a metal–carbon σ bond,[16] and it is clear that the factors which determine the direction of addition in these reactions are not fully understood.

Experimental Section

Measurements. The 100-MHz ^{1}H nmr spectra were run on a

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JEOL MH-100 spectrometer. Proton-decoupled ^{31}P spectra were obtained on a JEOL C-60 spectrometer using a CAT program on a PDP8-I computer. Analyses and molecular weight measurements were performed by the Microanalytical Service in the Research School of Chemistry and the John Curtin School of Medical Research, Australian National University, by Miss Brenda Stevenson and Dr. Joyce Fildes and associates.

Materials. AR grade solvents were used without further purification. $Pt(CH_3)_2(SP)$ (I) and $PtCl(CH_3)(SP)$ were prepared by reaction of SP with $Pt(CH_3)_2(COD)$ and $PtCl(CH_3)(COD)$, respectively.[17]

Preparation of $PtI(CH_3)(SP)$. A large excess (0.19 g) of sodium iodide was added to a solution of $PtCl(CH_3)(SP)$ (0.10 g) in acetone (30 ml), and the mixture was refluxed for 3 hr. After evaporation to dryness under reduced pressure, the residue was extracted with dichloromethane. The solution was filtered and, after addition of hexane, concentrated to give $PtI(CH_3)(SP)$ (II) as a pale yellow solid (87.5% yield). The complex was dried at room temperature under vacuum. *Anal.* Calcd for $C_{21}H_{20}IPPt$: C, 40.3; H, 3.2; I, 20.3; P, 5.0; mol wt 625. Found: C, 39.9; H, 3.4; I, 20.2; P, 5.3; mol wt (vpo, $CHCl_3$, 25°) 645. ^1H nmr spectrum (δ, $CDCl_3$, ppm downfield from TMS): *Pt*-CH_3 (doublet with satellites), 1.27, $|^2J_{Pt-CH_3}| = 74$ Hz, $|^3J_{P-Pt-CH_3}| = 4.5$ Hz; H_A (doublet with satellites), 5.42, $|J_{Pt-H_A}| = 43$ Hz; H_B (doublet of doublets, with satellites), 3.79, $|J_{Pt-H_B}| = 36$ Hz, $|J_{P-H_B}| = 1.5$ Hz; H_C (doublet of doublets, with satellites), 6.08, $|J_{Pt-H_C}| = 32$ Hz; $|J_{H_AH_B}| < 1$ Hz; $|J_{H_BH_C}| = 14$ Hz; $|J_{H_AH_C}| = 8.5$ Hz. ^{31}P nmr spectrum (CH_2Cl_2): singlet at 26.7 ppm downfield from external 85% H_3PO_4, with satellites, $|^1J_{Pt-P}| = 4018$ Hz.

Reaction of $Pt(CH_3)_2(SP)$ (I) with Iodine. Iodine (0.045 g, 0.177 mol) was added to $Pt(CH_3)_2(SP)$ (0.09 g, 0.175 mmol) dissolved in dichloromethane (5 ml) to give a bright orange solution. It was evaporated under reduced pressure and the resulting orange oil was recrystallized from dichloromethane-hexane to give a yellow solid, identified by its nmr spectrum as $PtI(CH_3)(SP)$ (II) (85% yield).

Reaction of $Pt(CH_3)_2(SP)$ (I) with Iodomethane. A solution of $Pt(CH_3)_2(SP)$ (I) (0.5 g, 0.97 mmol) in dichloromethane (20 ml) was treated with iodomethane (0.5 ml, 7.9 mmol). The solution was allowed to stand for 2 days and then evaporated under reduced pressure to give a colorless oil. The ^1H nmr spectrum of part of this oil in $CDCl_3$ showed a complex pattern in the region δ 0–2.5 ppm but no peak characteristic of III at δ 2.56 ppm.

The oil was dissolved in chloroform and allowed to stand for 1 week, and again the solution was evaporated under reduced pressure. The ^1H nmr spectrum of the residue showed that it consisted predominantly of a mixture of $[PtI(CH_3)_3]_4$ (approximately 20%), $PtI(CH_3)(SP)$ (II) (approximately 40%), and III (approximately 40%).

A chromatography column was prepared with a suspension of Florisil in *n*-pentane, and the mixture was introduced onto the column in solution in a small volume of dichloromethane. The column was then eluted with *n*-pentane–dichloromethane mixtures, the proportion of dichloromethane being gradually increased. Initial fractions contained $[PtI(CH_3)_3]_4$ (9:1 *n*-pentane–dichloromethane). Later fractions (1:2 *n*-pentane–dichloromethane) contained $PtI(CH_3)(SP)$ (II) and then, only partially separated from II, III. Samples rich in III were fractionally crystallized from chloroform–*n*-hexane, and the less soluble fractions were combined. Recrystallization from $CHCl_3$–hexane, followed by drying under vacuum, gave a chloroform solvate of III approximately 90% pure, with II present as an impurity. *Anal.* Calcd for $C_{22}H_{22}IPPt \cdot {}^1/_{10}CHCl_3$: C, 40.75; H, 3.4; Cl, 1.6; I, 19.5; P, 4.8. Found: C, 40.3; H, 3.8; Cl, 1.6; I, 19.8; P, 4.6. ^1H nmr spectrum (δ, $CDCl_3$, ppm downfield from TMS): *Pt*-CH_3 (doublet with satellites), 1.47, $|^2J_{Pt-CH_3}| = 72.5$ Hz, $|^3J_{P-Pt-CH_3}| = 4.5$ Hz; *C*-CH_3 (singlet with satellites), 2.56, $|J_{Pt-CH_3}| = 15.5$ Hz; H_A (singlet with satellites), 5.80, $|J_{Pt-H_A}| = 41$ Hz; H_B (singlet with satellites), 3.95, $|J_{Pt-H_B}| = 38.5$ Hz. ^{31}P nmr spectrum: singlet at 21.4 ppm downfield from H_3PO_4, with satellites, $|^1J_{Pt-P}| = 4108$ Hz.

When iodomethane (5 ml, 79 mmol) was added to a solution of $Pt(CH_3)_2(SP)$ (0.707 g, 1.4 mmol) in chloroform (20 ml) and the solution was allowed to stand 3 weeks, the major product was $[PtI(CH_3)_3]_4$ and no formation of III was detected. However, when iodomethane (0.014 ml, 0.22 mmol) was added to a solution of I (0.058 g, 0.11 mmol) in $CDCl_3$ (0.4 ml) in an nmr tube and the reaction was followed over several days by ^1H nmr, peaks corresponding to I were observed to decrease slowly, with a corresponding increase in peaks due to $[PtI(CH_3)_3]_4$, II, and III.

Acknowledgments. We thank Mr. J. Chan for preparing the ligand SP, Mr. C. Arandjelovic for running the ^{31}P nmr spectra, and a referee for helpful comments.

Registry No. I, 39530-95-5; II, 52699-07-7; III, 52699-08-8; $PtCl(CH_3)(SP)$, 52730-54-8.

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A Nickel(IV) Complex of the $B_8CH_9{}^{3-}$ Ligand

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The first reported monocarbon carborane compounds of Ni(IV) were anionic bis complexes of the carbollide ion, $B_{10}CH_{11}{}^{3-}$, and some of its substituted derivatives.[1] We have recently reported neutral η-cyclopentadienylnickel(IV) complexes of the carbollide ligand[2] and also neutral bimetallic monocarbon complexes of the $B_7CH_8{}^{5-}$ ion containing formal $(\eta\text{-}C_5H_5Co)^{2+}$ and $(\eta\text{-}C_5H_5Ni)^{3+}$ units.[3] We now report a novel nickel(IV) complex of the $(\eta\text{-}1\text{-}B_8CH_9)^{3-}$ ligand, η-cyclopentadienyl-η-nonahydro-1-carba-*nido*-nonaboratonickel(IV),[4] constituting the first *closo*-metallocarborane in which a metal is unambiguously bound to a B_4 face.[5] This also constitutes the first existence of a "B_8C" fragment, as there are no known monocarbon carboranes or carborane anions containing eight boron atoms. The ligand is the third in a series of $B_nCH_{n+1}{}^{3-}$ carborane anions ($n = 7$ and 10 are known[1,2,6]), and the η-cyclopentadienyl complex is the second homolog in a series of neutral $C_5H_5Ni^{IV}B_nCH_{n+1}$ complexes.[2] These compounds are of particular interest since they obey the proposed[7] $2n + 14$ electron rule for closo n-vertex polyhedral heteroboranes and are thus, as neutral complexes, predicted to be stable species which will undergo polyhedral rearrangements (as found for $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}7\text{-}B_{10}CH_{11})^2$) and a variety of other reactions characteristic of the $B_nC_2H_{n+2}$ carboranes and cobaltacarboranes.[7b]

Results and Discussion

In a recent paper[2] on the synthesis of $(\eta\text{-}C_5H_5)Ni^{IV}(\eta\text{-}7\text{-}$

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(5) This has been proposed[3] for the related complex $(C_5H_5)_2Co^{III}Ni^{IV}B_7CH_8$ but the spectroscopic data do not uniquely define the structure; there have also been reports of *closo*-metallocarboranes containing B_2C_2 bonding faces [see W. J. Evans, G. B. Dunks, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 95, 4565 (1973); R. N. Grimes, *et al.*, *ibid.*, 96, 3090 (1974)] and a *nido*-metallocarborane containing a B_4 face [see V. R. Miller and R. N. Grimes, *J. Amer. Chem. Soc.*, 95, 5078 (1973)].

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