Acknowledgment. We thank Mr. Akira Mizuno and Mr. Yoshihisa Toda at the Materials Science & Analysis Laboratories, Mitsui Petrochemical Industry, Ltd., for ^{31}P NMR measurements. We also thank TOSOH AKZO Corp. for a kind gift of alkylaluminums. This work was supported by Grants-in-Aid for Scientific Research (No. 02640479) and for Priority Area of Organic Unusual Valency (No. 03233222) from the Ministry of Education, Science and Culture of Japan.

Registry No. 1, 14221-01-3; 2, 33309-88-5; 3, 82916-00-5; 4, 75172-21-3; 5, 60885-30-5; 6, 70316-76-6; 7, 63455-39-0; 8, 138695-22-4; 9, 138695-23-5; 10, 138695-24-6; 11, 138695-25-7; $PhC(O)P(O)(OEt)_2$, 3277-27-8; $tolC(O)P(O)(OEt)_2$, 2942-54-3; MeC_6H_4-*p*-$C(O)P(O)(OEt)_2$, 16703-95-0; ClC_6H_4-*p*-$C(O)P(O)(OEt)_2$, 10570-46-4; $PhC(O)P(O)(OMe)_2$, 18106-71-3; $MeC(O)P(O)(OEt)_2$, 919-19-7; $MeC(O)P(O)(OMe)_2$, 17674-28-1; $EtC(O)P(O)(OEt)_2$, 1523-68-8; $EtC(O)P(O)(OMe)_2$, 51463-65-1; $PhP(O)(OEt)_2$, 1754-49-0; $tolP(O)(OEt)_2$, 1754-46-7; $MeOC_6H_4$-*p*-$P(O)(OEt)_2$, 3762-33-2; ClC_6H_4-*p*-$P(O)(OEt)_2$, 2373-43-5; $PhP(O)(OMe)_2$, 2240-41-7; $MeP(O)(OEt)_2$, 683-08-9; $MeP(O)(OMe)_2$, 756-79-6; $EtP(O)(OEt)_2$, 78-38-6; $EtP(O)(OMe)_2$, 6163-75-3; $tolC(O)P(O)(OMe)_2$, 33493-30-0; $tolP(O)(OMe)_2$, 6840-25-1; *trans*-$PdEt_2(PMe_3)_2$, 124717-55-1.

Notes

Double Insertion of Methylene into Nickel–Phosphorus Bonds: Synthesis and Structure of $[Ni(CH_2PPh_2CH_2PPh_2)_2][Br]_2$

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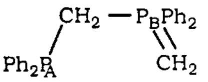
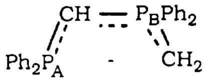
Received August 21, 1991

Summary: The new nickel phosphorus ylide complex, $[Ni(CH_2PPh_2CH_2PPh_2)_2][Br]_2$ (1) has been prepared by the reaction of $Ni(COD)_2$, dppm (bis(diphenylphosphino)methane), and CH_2Br_2. The complex crystallizes from DMSO as 1·2DSMO: triclinic space group $P\bar{1}$, $a = 9.972$ (2) Å, $b = 12.061$ (2) Å, $c = 12.675$ (2) Å, $\alpha = 114.19$ (1)°, $\beta = 100.71$ (1)°, $\gamma = 91.45$ (1)°, $V = 1357.6$ Å^3 ($Z = 1$). Complex 1 can be reversibly deprotonated by 2 equiv of $NaNH_2$ to afford $Ni(CH_2PPh_2CHPPh_2)_2$ (2) and reprotonated by HBr.

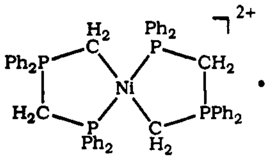
Nickel complexes with chelating phosphorus ylide ligands are of considerable interest as catalysts for olefin homologation and polymerization.[1] A nickel ylide complex reported by Keim and co-workers[2] is a highly active catalyst for the Shell higher olefins process (SHOP).[3] A variety of different synthetic routes to modified chelating phosphorus ylide nickel catalysts have been described.[4-8] We now report a remarkably straightforward preparation of a new nickel ylide complex $[Ni(CH_2PPh_2CH_2PPh_2)_2][Br]_2$ (1). Complex 1 can be reversibly deprotonated to afford the neutral product $Ni(CH_2PPh_2CHPPh_2)_2$ (2), which was prepared earlier via a different procedure by Schmidbaur.[4] Results of an X-ray crystallographic study of 1 provide the opportunity to compare the characteristics of (methylenediphenylphosphino)(diphenylphosphino)methane (A) and its deprotonated ylide anion (B) as chelating ligands to the same metal.


(A)


(B)

The complex $[Ni(CH_2PPh_2CH_2PPh_2)_2][Br]_2$ (1) was prepared by addition of 2 equiv of dppm (bis(diphenylphosphino)methane) to 1 equiv $Ni(COD)_2$[9,10] (COD = 1,5-cyclooctadiene) at −20 °C in toluene, followed by addition of 2 equiv of CH_2Br_2. The yellow solid was filtered out, washed with diethyl ether, and dried under vacuum to obtain 1 in yields approaching the theoretical limit of 50% based on $Ni(COD)_2$ (1 equivalent of $Ni(COD)_2$ is oxidized by CH_2Br_2) (eq 1). The $^{31}P\{^1H\}$ NMR spectrum

$$2\,Ni(COD)_2 + 2\,dppm + 2\,CH_2X_2 \xrightarrow[\text{toluene}]{}$$



$\cdot 2Br^- + NiX_2(COD) + 3\,COD$ (1)

1

(X = Br, I)

of 1 in DMSO-d_6 consists of two approximate triplets centered at 47.87 and 32.31 ppm with $J(AB) \approx J(AB') =$

[†] Address correspondence pertaining to crystallographic studies to this author.

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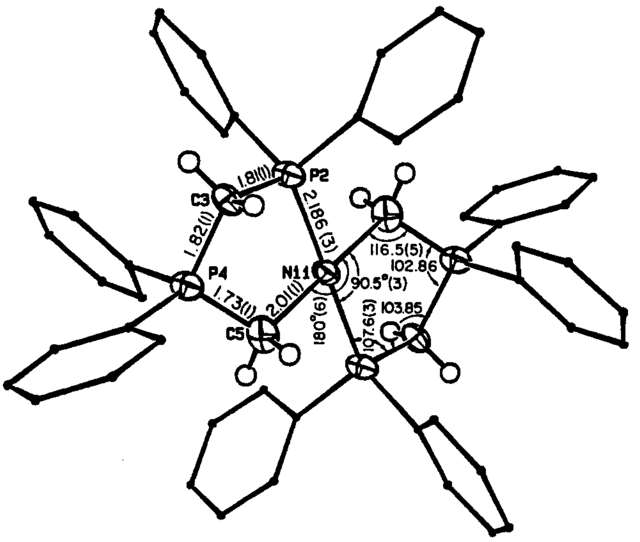


Figure 1. ORTEP drawing of $[Ni(CH_2PPh_2CH_2PPh_2)_2]^{2+}$, the molecular ion of 1, with selected bond distances and angles.

56.5 Hz. The ^1H NMR spectrum reveals both types of methylenes. The ylide protons are observed at δ 1.38 (m, 4 H), and the normal methylene protons appear as a pseudotriplet at δ 4.40 (4 H). Coordinated phosphorus ylides normally display methylene proton chemical shifts ranging from 8.25 to 1.2 ppm.[4,11,12] The ylide carbons of 1 are apparently introduced by insertion of methylene into the nickel–phosphorus bonds of coordinated dppm. Insertion of methylene into metal–phosphorus bonds to form metal ylide complexes was first reported in 1979.[13] Zerovalent $Pt(PR_3)_4$ complexes undergo oxidative addition of dihalomethanes which lead via haloalkylmetal intermediates to ylide complexes.[14,15] Methylene may also be inserted into M–P and M–S bonds by reactions with diazomethane.[11,16] Complex 1 is the first example of multiple methylene insertion between nickel and diphosphine ligands to form a metallocyclic phosphorus ylide complex.

Single crystals of 1 were obtained by slow diffusion of diethyl ether into a DMSO solution of 1. An ORTEP drawing of the molecular dication of 1 with bond distances and angles is presented in Figure 1. The nickel atom lies on a center of symmetry and has approximate square-planar geometry, chelated by two $CH_2PPh_2CH_2PPh_2$ phosphine ylides.

One methylene proton of each chelating ylide ligand of 1 can be reversibly deprotonated. Treatment of 1 with 2 equiv of $NaNH_2$ affords the neutral complex $Ni(CH_2PPh_2CHPPh_2)_2$ (2) in 85% yield. Complex 2 was first reported by Schmidbaur and co-workers by the addition of two equiv of $Na[CH_2PPh_2CHPPh_2]$ to $NiCl_2(PMe_3)_2$.[4] The $^{31}P\{^1H\}$ NMR spectrum of 2 in CD_2Cl_2-d_2 recorded at 80.96 MHz consists of an AA′BB′ system centered at δ 41.19, Figure 2. Our $^{31}P\{^1H\}$ spectrum appears different from that reported by Schmidbaur due to the different fields (80.96 vs 36.43 MHz) employed to record the second-order spectrum. The $^{31}P\{^1H\}$ NMR spectra of 2, reported by us and by Schmidbauer,[4] are both described by the coupling constants: $^2J(P_AP_{A'})$ = 271.7 Hz, $^2J(P_AP_B)$ = $^2J(P_{A'}P_{B'})$ = 155.9 Hz, $^3J(P_AP_{B'})$ = $^3J(P_{A'}P_B)$ = 34.7 Hz, $^4J(P_BP_{B'})$ = 0.2 Hz. Complex 2 is readily reprotonated by 2 equiv of HBr to return 1 quantitatively (eq 2).

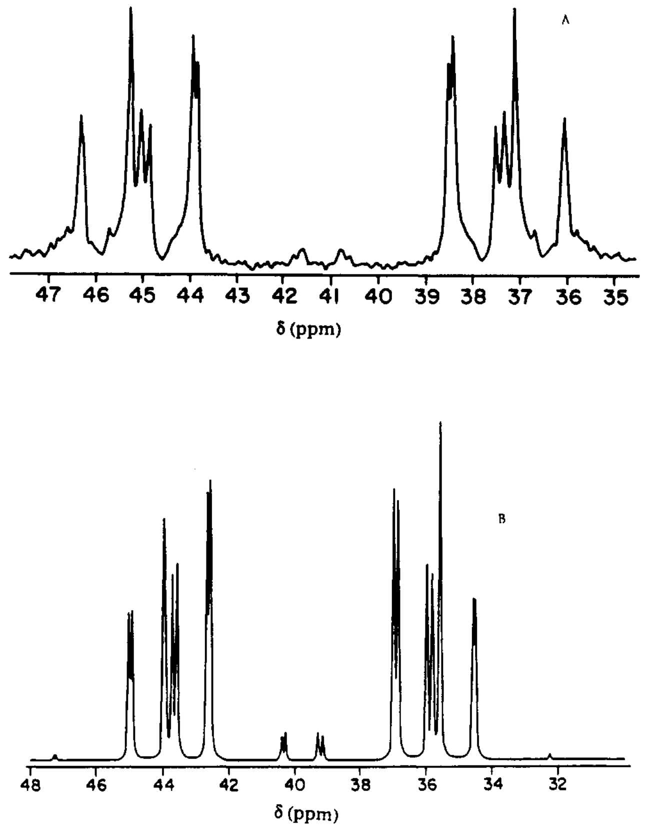
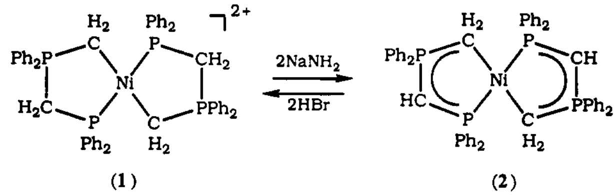
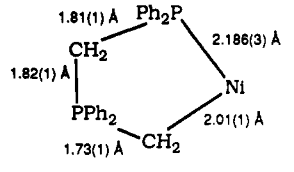


Figure 2. $^{31}P\{^1H\}$ NMR spectra of $Ni(CH_2PPh_2CHPPh_2)_2$ (2) at 81 MHz: (a) observed spectrum; (b) simulated spectrum described by $^2J(P_AP_{A'})$ = 271.7 Hz, $^2J(P_AP_B)$ = $^2J(P_{A'}P_{B'})$ = 155.9 Hz, $^3J(P_AP_{B'})$ = $^3J(P_{A'}P_B)$ = 34.7 Hz, and $^4J(P_BP_{B'})$ = 0.2 Hz.

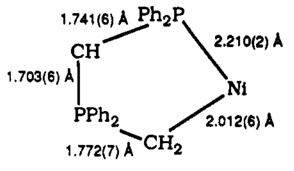


(2)

The structure of 1[17] together with the structural data for 2, reported earlier by Schmidbaur,[4] provides the interesting opportunity to compare the ylide (A) and ylide anion (B) as ligands. A summary comparison of the important metrical parameters for the chelate rings of the two structures is as follows:



1



2

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(17) X-ray-quality crystals of 1 were obtained by slow diffusion of ether into DMSO solution. The complex crystallized as 1·2DMSO in the triclinic space group $P\bar{1}$, with a = 9.972 (2) Å, b = 12.061 (2) Å, c = 12.675 (2) Å, α = 114.19 (1)°, β = 100.71 (1)°, γ = 91.45 (1)°, V = 1357.6 Å^3, Z = 1, and d_{calcd} = 1.43 g/cm^3 for the formula $C_{56}H_{60}Br_2NiO_2P_4S_2$. Crystal dimensions were 0.17 × 0.17 × 0.11 mm. A total of 3531 unique data were collected over the h,k,l limits −10 to +10, −12 to +11, and 0 to 13. The structure was solved by MULTAN–least squares–Fourier methods and was refined to R and R_w values of 0.058 and 0.063 for 289 variables with $I > 3.0\sigma(I)$. All programs were from the Enraf-Nonius SDP package. All calculations were performed on a micro-VAX computer.

A significant shortening of both methine carbon–phosphorus bond distances for 2 compared to the methylene–phosphorus bonds of 1 are consistent with the delocalized partial multiple P–C bond character expected upon deprotonation of 1. The ylide carbon–phorphorus bond distance of 1, *d*(P4–C5) = 1.73 (1) Å, indicates significant double-bond character.[4] The corresponding carbon–phosphorus bond distance of 2 is slightly longer, 1.772 (7) Å, again consistent with delocalized vs localized carbon–phosphorus ylide double bonds in 2 vs 1, respectively. This delocalization has no apparent effect on the ylide carbon–nickel bond distances but does increase the phosphorus–nickel bond distance of 2 compared to 1.

A survey of the chemistry of 1 with CO, CO_2, and ethylene indicates no significant reactivity at 1 atm. Our ongoing efforts are based on employing the new phosphorus ylide, (methylenediphenylphosphino)(diphenylphosphino)methane (A), as a ligand in monochelate complexes related to existing nickel olefin homologation and polymerization catalysts.[1–7]

Acknowledgment is made to the National Science Foundation (Grants CHE-8707963 and CHE-9016513) for support of this work.

Registry No. 1·2DMSO, 138783-56-9; 2, 133009-19-5; Ni(COD)$_2$, 1295-35-8.

Supplementary Material Available: Textual presentation of experimental procedures, tables of experimental details and results, torsional angles, positional and isotropic thermal parameters, general temperature factor expressions, and bond distances and angles, and a figure showing observed and calculated $^{31}P\{^1H\}$ NMR spectra at 81 MHz for 1 (18 pages); a listing of observed and calculated structure factors for 1 (12 pages). Ordering information is given on any current masthead page.

Synthesis, Reactivity, and Molecular Structure of [(phenylsilatrane)Mn(CO)$_2$P(OMe)$_3$]ClO$_4$

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Summary: [(phenylsilatrane)Mn(CO)$_2$P(OMe)$_3$]ClO$_4$ (2) has been prepared by reaction of [(phenylsilatrane)Mn(CO)$_3$]ClO$_4$ (1) with P(OMe)$_3$. Compound 2 undergoes regioselective reactions with MeLi, PhLi, and PhMgBr in CH_2Cl_2. However, 2 does not react regioselectively with carbanions in THF. Complex 2 crystallizes in the monoclinic space group $P2_1/n$ with a = 16.354 (4) Å, b = 6.585 (1) Å, c = 22.165 (5) Å, β = 97.52 (1)°, V = 2366.7 Å^3, and Z = 4. The structure was refined to R = 0.051 and R_w = 0.051 for all 4741 reflections.

In recent studies we and others have established the utility of (arene)Mn(CO)$_3^+$ cations in difunctionalizing cyclohexadienes by nucleophilic addition to coordinated arenes.[2] The factors influencing the observed regiochemistry of nucleophilic attack are very important and need clarification. The regioselectivity for the addition of nucleophiles to $(C_6H_5X)Cr(CO)_3$ can generally be controlled not only by the substituent on the arene but also by the conformation.[3] With alkyl substituents, while the expected meta attack predominates for small X (Me and Et), reaction at the para position increases with increasing steric bulk of X until it becomes the only site of attack for X = CH^tBu_2.[4] This unusual observation has been rationalized in terms of the conformational preferences of the Cr(CO)$_3$ group.[3] We expect that the regiochemistry of (arene)Mn(CO)$_3^+$ would be very similar to that of (arene)Cr(CO)$_3$.[5]

Recently we reported the use of phenylsilatrane as a π-coordinating ligand for transition metals.[6] The chemistry of the Cr(CO)$_3$ and Mn(CO)$_3^+$ derivatives of phenylsilatrane has been studied.[6a,b] The Mn(CO)$_3^+$ derivative 1 undergoes regioselective reaction with RMgBr (R = Ph, Et, Et) in CH_2Cl_2 to give [η^5-1-(N(CH$_2$CH$_2$O)$_3$Si)-6-(R)-C$_6$H$_5$]Mn(CO)$_3$ and RMgBr (R = Ph, Me, Et) and LiR (R = CH$_2$CO$_2$CMe$_3$, CH$_2$CN, $\overline{\mathrm{CHC(CH_2)_3S}}$) in THF to yield [$\eta^5$-3-(N(CH$_2CH_2$O)$_3$Si)-6-(R)-C$_6H_5$]Mn(CO)$_3$. The selectivity of the nucleophile addition to 1 is strongly dependent on the nucleophile and reaction medium. This special regioselectivity of compound 1 would partially come from the staggered conformation of metal carbonyls.[6c]

To elucidate the possible effects of various factors that may influence the regioselectivity of the carbanion addition, we have prepared [(N(CH$_2$CH$_2$O)$_3$SiC$_6$H$_5$)Mn(CO)$_2$P(OMe)$_3$]ClO$_4$ (2) from 1 and studied the reactivity of compound 2. In this note we report the synthesis of

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