Inorg. Chem. **1991**, *30*, 4271–4275

$(CPI)_6Cl$, 133471-53-1; $NH_4{}^{99}TcO_4$, 34035-97-7; $^{99}Tc(CNC(CH_3)_2COOH)_6Cl$, 133471-54-2; $^{99}Tc(CNC(CH_3)_2COOH)_5(CPI)Cl$, 133495-00-8; *trans*-$^{99}Tc(CNC(CH_3)_2COOH)_4(CPI)_2Cl$, 133471-55-3; *cis*-$^{99}Tc(CNC(CH_3)_2COOH)_4(CPI)_2Cl$, 133574-95-5; *mer*-$^{99}Tc(CNC(CH_3)_2COOH)_3(CPI)_3Cl$, 133471-56-4; *fac*-$^{99}Tc(CNC(CH_3)_2COOH)_3(CPI)_3Cl$, 133574-96-6; *trans*-$^{99}Tc(CNC(CH_3)_2COOH)_2(CPI)_4Cl$, 133471-57-5; *cis*-$^{99}Tc(CNC(CH_3)_2COOH)_2(CPI)_4Cl$, 133574-97-7; $^{99}Tc(CNC(CH_3)_2COOH)(CPI)_5Cl$, 133471-58-6; $^{99}Tc(CNC(CH_3)_2COONa)_6{}^+$, 133495-01-9; trichloromethyl chloroformate, 503-38-8.

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Structure and Metal Coordination of the Diphosphane 2,2′-Bis((diphenylphosphino)methyl)-1,1′-biphenyl ("BISBI")

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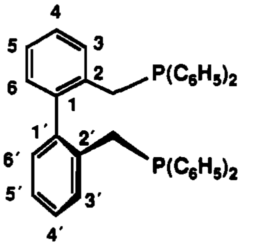
2,2′-Bis((diphenylphosphino)methyl)-1,1′-biphenyl (1, BISBI) crystallizes in the orthorhombic space group $Pca2_1$, with a = 22.845 (1) Å, b = 13.3796 (6) Å, c = 19.642 (1) Å, V = 6004 Å^3, and Z = 8. The X-ray crystal structure analysis of 1 revealed two independent molecules in the unit cell. [2,2′-Bis((diphenylphosphino)methyl)-1,1′-biphenyl]tetracarbonyl-molybdenum (3), prepared in 47% yield from (norbornadiene)$Mo(CO)_4$ and the ligand BISBI, was also structurally characterized. Crystals of $3\cdot 0.92CH_2Cl_2$, grown from methylene chloride at room temperature, are monoclinic, with space group $P2_1/n$, a = 15.444 (1) Å, b = 13.957 (1) Å, c = 18.503 (1) Å, β = 92.55 (1)°, V = 3984 Å^3, and Z = 4. The structure of 3 shows a nearly octahedral coordination of the molybdenum atom, with the diphosphane ligand in cis positions. The P–Mo–P′ "bite angle" is 103.54 (2)°. 3 belongs to the very few known complexes that exhibit nine-membered, metal-containing ring systems of diphosphane ligands. BISBI can adopt to any coordination geometry with small (90°) and large "bite angles" (180°) upon *intra*molecular (chelating) metal attachment while there is no experimental evidence for *inter*molecular complexation.

Introduction

It is well-known that increasing steric bulk of monodentate ligands leads to higher regioselectivity in hydroformylation.[1] Bidentate phosphanes with large P–M–P′ "bite angles" thus should improve the *n*/iso ratio in this reaction. In a recent paper, Casey and coworkers[2] reported on the coordination chemistry of the novel ligand 2,2′-bis((diphenylphosphino)methyl)-1,1′-biphenyl (1, "BISBI") in a pentacoordinated iron complex. It was found that this particular diphosphane has a P–M–P′ bite angle greater than 120°. In the context of our ongoing work on hydroformylation,[3,4] we were interested in the molecular structure of the free ligand as compared with its conformation when membered in a penta- or hexacoordinated metal complex. To this end, we prepared an octahedral molybdenum(0) complex. This work is reported in the present paper.



1

Results

A. Crystal Structure of the Ligand. BISBI is a relatively new diphosphane that has been described in several patents of Kodak.[5] A new convenient synthetic route is now available from our own laboratory.[4] Single crystals of compound 1 were grown from an ethanol solution at room temperature. The X-ray crystal structure (Figure 1) shows two independent molecules with different conformations in the unit cell. Molecule A has a smaller interplanar angle of the biphenyl moiety (dihedral angle for molecule A is 69.87°, and it is 76.97° for molecule B defined by C51–C56–C66–C61). As a consequence the P⋯P′ distances are 6.73 Å for molecule A and 6.86 Å for B. While the conformations around P1A and P1B are similar for both molecules, they are quite different at the atoms P2A and P2B as shown in Figure 1. The phenyl groups attached to these phosphorus atoms are twisted in an opposite manner. The coordination geometry around all phosphorus atoms is as expected for sp^3 hybridization including a lone pair. Corresponding bond distances and bond angles of A and B are nearly equal. These data fall in the normal range for P–C(aliphatic) and P–C(aromatic) bonds.

From reflection statistics and systematic absences, the acentric space group $Pca2_1$ clearly was determined, although a refinement in the enantiomorphic setting gave no significant change in the R values. However, both independent molecules have different conformations and cannot be symmetry related.

The NMR data provide information about the structure of the free ligand 1 in solution. The $^{13}C\{^1H\}$ NMR spectrum shows 14 different signals in the typical aromatic shift region due to the axial chirality of the molecule. The two phenyl rings directly attached to the phosphorus atom are *non*equivalent and give rise to separate signals for each carbon atom, indicating that inversion at the phosphorus atom is very slow on the NMR time scale. The

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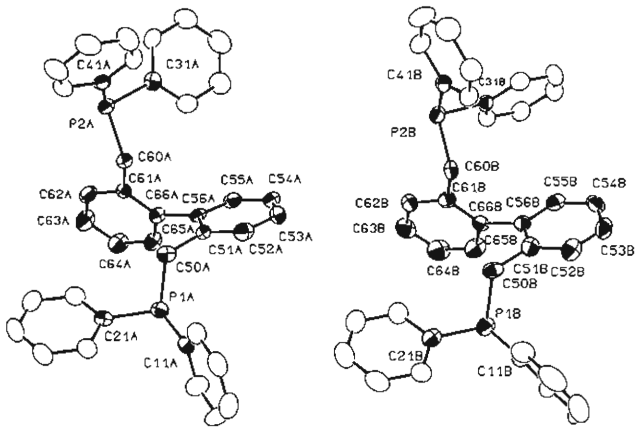


Figure 1. ORTEP diagrams of **1**, showing the two different molecules A (left) and B (right). Thermal ellipsoids are drawn at the 50% probability level, with hydrogen atoms omitted for clearity.

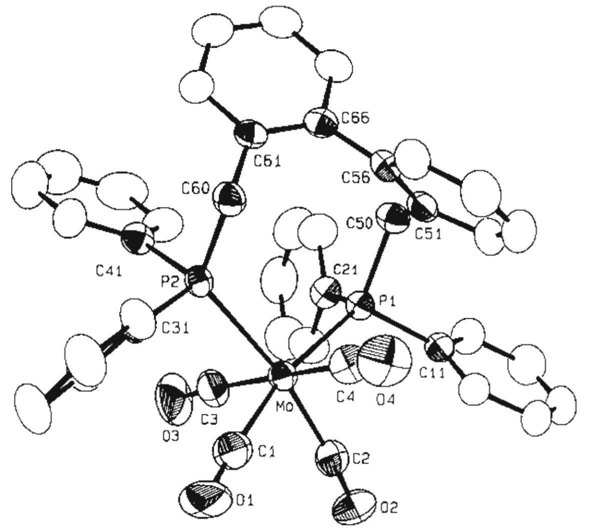


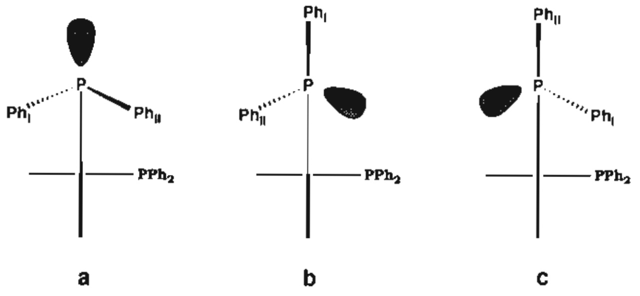
Figure 2. ORTEP view of **3** with 50% probability ellipsoids, with hydrogen atoms omitted for clearity.

relationship between asymmetry of the biphenyl system and the rotational isomers is illustrated in Chart I.

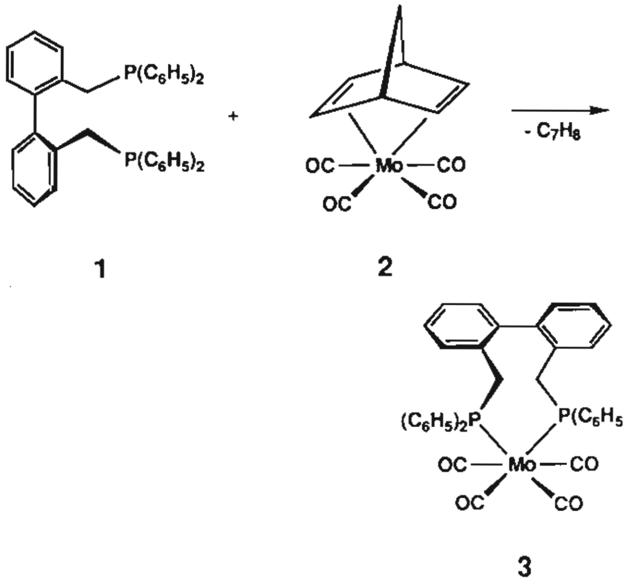
In each of the three rotamers, phenyl group I has a different environment than phenyl ring II. In a similar case, the nonequivalence of two methyl groups was noted.[6] At the same time, the phenyl groups are freely rotating around the P–C(ipso) bond, consequently generating only four signals in the ^{13}C NMR for each ring.

B. Synthesis and Crystal Structure of a BISBI–Molybdenum(0) Complex. BISBI was reported to have special selectivity effects in the homogeneous rhodium-catalyzed hydroformylation of propene.[5a] The high selectivity observed in this process indicates a crowded ligand environment at the metal, which directs the olefin

Chart I. Conformations of the Ligand **1** (Ph = C_6H_5)



Scheme I



toward unbranched rather than branched products. BISBI thus appears to become a ligand of industrial use. It is therefore of continued interest to study the chelating effect of this and related ligands and to determine the P–M–P′ bite angle.

Reaction of BISBI with [bicyclo[2.2.1]hepta-2,5-diene]tetracarbonylmolybdenum(0) (**2**) in toluene at 110 °C yields (BISBI)Mo$(CO)_4$ (**3**) as a pale yellow, air-stable solid (47%) (Scheme I).

Single crystals of **3** were grown from a CH_2Cl_2/*n*-hexane solution (1/3 vol/vol). The molecular structure was determined by means of X-Ray diffraction techniques (Figure 2). The refinement was carried out with an occupancy factor of 0.92 for methylene chloride, which has been borrowed from elemental analysis. The complex is one of the few cases of nine-membered ring systems without further heteroatoms in the ligand's backbone. The coordination sphere around the metal center is nearly octahedral, with the P–Mo–P′ bite angle of the cis-coordinated diphosphane being 103.54 (2)°. The interplanar angle of the biphenyl system is 117.73°; the P···P′ distance through space is 4.03

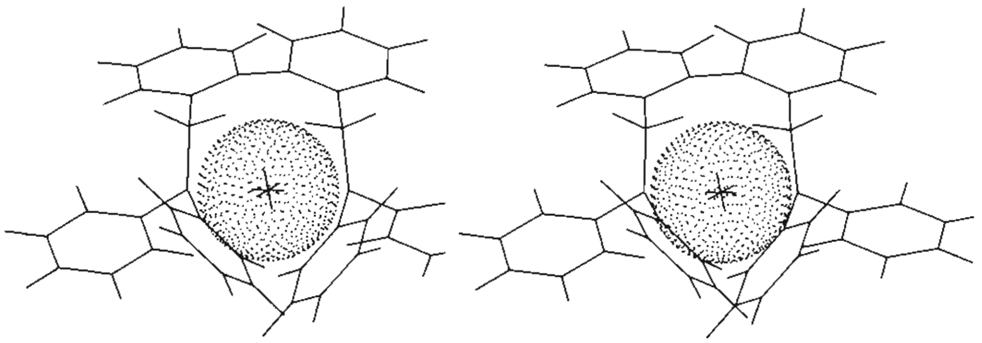


Figure 3. Stereoview of calculated trans-spanning "BISBI".

Table I. Crystallographic Data and Summary of Data Collection and Refinement Parameters for 2,2′-Bis((diphenylphosphino)methyl)-1,1′-biphenyl (**1**) and [2,2′-Bis((diphenylphosphino)methyl-1,1′-biphenyl]tetracarbonylmolybdenum (**3**)

	1	3
formula	$C_{38}H_{32}P_2$	$C_{42}H_{32}MoO_4P_2\cdot 0.92CH_2Cl_2$
fw	550.62	843.5
crystal system	orthorhombic	monoclinic
space group	$Pca2_1$ (No. 29)	$P2_1/n$ (No. 14)
temp, K	173 ± 3	298 ± 1
a, Å	22.845 (1)	15.444 (1)
b, Å	13.3796 (6)	13.957 (1)
c, Å	19.642 (1)	18.503 (1)
β, deg		92.55 (1)
Z	8	4
V, Å^3	6004	3984
d_{calc}, g cm^{-3}	1.218	1.406
μ, cm^{-1}	14.9	51.0
R^a	0.056	0.052
$R_w{}^b$	0.044	0.054
extinction ($F_c = F_c(1 - \epsilon F_c{}^2/(\sin\theta))$, ϵ	3.93×10^{-7}	no

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ with weighting scheme $(1/\sigma^2(F_o))$.

Å. The four carbonyl groups occupy two axial and two equatorial positions; the C–Mo–C angles range from 82.49 (9) to 95.15 (9)°.

Each of the carbonyl groups can be seen in the $^{13}C\{^1H\}$ NMR spectrum, so there is no indication of fluxionality at room temperature. The axial carbonyl groups show a triplet at δ 208.7 ppm (J_{PC} = 9.8 Hz), while the equatorial carbonyl groups generate a virtual quintet (AXX′ spin system with small $J_{xx'}$ at δ 214.8 ppm. Analysis of this higher order spectrum gives a calculated $J_{PP'}$ = 30 Hz.[7] This small $J_{PP'}$ is consistent with the relatively small P–M–P′ angle of 103.54 (2)° resulting from the X-ray structure analysis. In the infrared spectrum, four carbonyl bands (ν(CO)) can be seen, as might be expected for the cis isomer of an octahedral complex $L_2M(CO)_4$. Every single proton of the biphenyl system can be assigned on the basis of selective ^1H–^1H-decoupling NMR experiments. The ortho protons (H6 and H6′) show a remarkable chemical shift to high field (δ 6.16 ppm), which can be explained by the twisting of the two phenyl groups around the C1–C1′ bond. These protons are very near to the π-electrons of the neighboring phenyl ring. This shielding effect leads to the observed unusual chemical shift. Note: the molecular mass of m/e = 758 and loss of four carbonyls can only be detected in the mass spectra upon employment of chemical ionization (CI) techniques.

Discussion

The X-ray structures of free and metal-coordinated BISBI shows that this particular diphosphane has a pronounced flexibility. The ligand can behave like other well-known diphosphanes (cis coordination). On the other hand, BISBI also forms complexes with unusually large "bite angles". Including the results of Casey et al.,[2] the P–M–P′ bite angle of BISBI in metal complexes now ranges from 103.5° (cis octahedral) to 152.0° (trans square pyramidal). The complex (BISBI)RhH(CO)[P(C_6H_5)$_3$], also synthesized in Casey's group,[8] displays a P–Rh–P′ angle for BISBI of 124.8(1)° (equatorial trigonal bipyramidal). There is also

Table II. Final Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **1** with Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c	U_{eq},^{a} Å^2	atom	x/a	y/b	z/c	U_{eq},^{a} Å^2
P1A	−0.25652 (5)	−0.21103 (8)	0	0.031	C65A	−0.1576 (2)	−0.3663 (4)	0.1171 (3)	0.036
P2A	−0.31227 (5)	−0.62397 (9)	0.18430 (9)	0.030	C66A	−0.2048 (2)	−0.4259 (3)	0.0956 (3)	0.029
P1B	−0.02731 (6)	0.3004 (1)	0.02925 (9)	0.036	C11B	−0.0105 (3)	0.3332 (4)	0.1176 (3)	0.041
P2B	0.04469 (6)	−0.10343 (9)	−0.1692 (1)	0.031	C12B	0.0444 (3)	0.3233 (4)	0.1470 (3)	0.050
C11A	−0.2814 (2)	−0.1556 (4)	−0.0808 (3)	0.032	C13B	0.0529 (4)	0.3498 (5)	0.2151 (4)	0.060
C12A	−0.3292 (2)	−0.1879 (4)	−0.1187 (3)	0.042	C14B	0.0083 (6)	0.3841 (6)	0.2528 (4)	0.066
C13A	−0.3437 (3)	−0.1388 (4)	−0.1790 (3)	0.048	C15B	−0.0461 (4)	0.3940 (5)	0.2246 (4)	0.059
C14A	−0.3121 (3)	−0.0593 (5)	−0.2023 (3)	0.055	C16B	−0.0566 (3)	0.3689 (4)	0.1574 (3)	0.049
C15A	−0.2659 (3)	−0.0262 (4)	−0.1651 (4)	0.058	C21B	0.0235 (2)	0.3794 (4)	−0.0189 (2)	0.034
C16A	−0.2495 (3)	−0.0747 (4)	−0.1047 (3)	0.051	C22B	0.0530 (2)	0.4615 (4)	0.0085 (3)	0.038
C21A	−0.3036 (2)	−0.1474 (3)	0.0622 (3)	0.032	C23B	0.0882 (2)	0.5217 (4)	−0.0329 (3)	0.046
C22A	−0.2968 (2)	−0.1743 (4)	0.1303 (3)	0.045	C24B	0.0940 (2)	0.5002 (5)	−0.1016 (3)	0.048
C23A	−0.3289 (3)	−0.1285 (4)	0.1814 (3)	0.053	C25B	0.0654 (3)	0.4205 (5)	−0.1282 (3)	0.048
C24A	−0.3678 (3)	−0.0533 (4)	0.1650 (3)	0.051	C26B	0.0298 (2)	0.3600 (4)	−0.0883 (3)	0.045
C25A	−0.3745 (2)	−0.0240 (4)	0.0977 (3)	0.043	C31B	−0.0129 (2)	−0.1856 (3)	−0.1351 (2)	0.029
C26A	−0.3421 (2)	−0.0707 (4)	0.0468 (3)	0.038	C32B	−0.0696 (2)	−0.1686 (4)	−0.1581 (3)	0.035
C31A	−0.2657 (2)	−0.7230 (4)	0.1483 (3)	0.032	C33B	−0.1157 (2)	−0.2254 (4)	−0.1337 (3)	0.037
C32A	−0.2733 (2)	−0.8193 (4)	0.1704 (3)	0.041	C34B	−0.1060 (2)	−0.3005 (4)	−0.0868 (3)	0.040
C33A	−0.2394 (3)	−0.8962 (4)	0.1458 (3)	0.050	C35B	−0.0497 (2)	−0.3187 (4)	−0.0642 (3)	0.042
C34A	−0.1954 (2)	−0.8758 (4)	0.0995 (4)	0.048	C36B	−0.0033 (2)	−0.2612 (4)	−0.0884 (3)	0.037
C35A	−0.1873 (2)	−0.7810 (4)	0.0782 (4)	0.051	C41B	0.1122 (2)	−0.1600 (4)	−0.1374 (3)	0.031
C36A	−0.2225 (2)	−0.7036 (4)	0.1016 (3)	0.047	C42B	0.1342 (2)	−0.1483 (4)	−0.0722 (3)	0.038
C41A	−0.3856 (2)	−0.6613 (3)	0.1551 (3)	0.028	C43B	0.1874 (2)	−0.1909 (4)	−0.0528 (3)	0.048
C42A	−0.4330 (2)	−0.6140 (4)	0.1863 (3)	0.039	C44B	0.2182 (2)	−0.2485 (5)	−0.0987 (4)	0.052
C43A	−0.4892 (2)	−0.6373 (4)	0.1671 (3)	0.044	C45B	0.1972 (3)	−0.2608 (5)	−0.1643 (4)	0.052
C44A	−0.4997 (2)	−0.7093 (4)	0.1194 (3)	0.043	C46B	0.1451 (2)	−0.2175 (4)	−0.1838 (3)	0.044
C45A	−0.4534 (2)	−0.7572 (4)	0.0884 (3)	0.044	C50B	0.0105 (2)	0.1773 (4)	0.0208 (3)	0.032
C46A	−0.3964 (2)	−0.7320 (4)	0.1064 (3)	0.036	C51B	−0.0271 (2)	0.0882 (4)	0.0409 (3)	0.034
C50A	−0.2908 (2)	−0.3381 (3)	0.0013 (3)	0.031	C52B	−0.0295 (2)	0.0564 (4)	0.1079 (3)	0.040
C51A	−0.2488 (2)	−0.4170 (3)	−0.0228 (2)	0.026	C53B	−0.0621 (2)	−0.0246 (4)	0.1263 (3)	0.041
C52A	−0.2476 (2)	−0.4484 (4)	−0.0899 (3)	0.036	C54B	−0.0941 (2)	−0.0773 (4)	0.0774 (3)	0.038
C53A	−0.2058 (2)	−0.5157 (4)	−0.1136 (3)	0.037	C55B	−0.0925 (2)	−0.0444 (4)	0.0108 (3)	0.035
C54A	−0.1637 (2)	−0.5517 (4)	−0.0702 (3)	0.037	C56B	−0.0606 (2)	0.0390 (3)	−0.0088 (3)	0.028
C55A	−0.1646 (2)	−0.5207 (3)	−0.0027 (3)	0.032	C60B	0.0351 (2)	0.0034 (4)	−0.1095 (2)	0.030
C56A	−0.2064 (2)	−0.4566 (3)	0.0226 (2)	0.025	C61B	−0.0186 (2)	0.0636 (4)	−0.1272 (3)	0.030
C60A	−0.3001 (2)	−0.5156 (3)	0.1259 (2)	0.028	C26B	−0.0242 (2)	0.1049 (4)	−0.1917 (3)	0.038
C61A	−0.2475 (2)	−0.4530 (3)	0.1439 (2)	0.026	C63B	−0.0733 (3)	0.1587 (4)	−0.2098 (3)	0.044
C62A	−0.2414 (2)	−0.4186 (4)	0.2104 (3)	0.037	C64B	−0.1184 (3)	0.1704 (4)	−0.1644 (3)	0.048
C63A	−0.1951 (3)	−0.3590 (4)	0.2304 (3)	0.043	C65B	−0.1136 (2)	0.1304 (4)	−0.1002 (3)	0.043
C64A	−0.1520 (2)	−0.3340 (4)	0.1828 (3)	0.041	C66B	−0.0639 (2)	0.0772 (3)	−0.0803 (2)	0.029

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

evidence that the compound (BISBI)IrH(CO)$_2$ contains a P–Ir–P′ angle much larger than 120° (large P–P′ coupling in the ^{31}P NMR).[8] In this context, our complex **3** shows an *unusually small bite angle* (103.54 (2)°). This indicates that the structures of chelating complexes are determined by other factors in addition to the rigidity of the ligand's backbone, for example the influence of the metal and its electronic configuration, the steric bulk of substituents bound to the donor atoms, the resulting chelate size and, in case of ionic complexes, the counterion. In view of these effects it appears necessary to synthesize a complex with trans-coordinating BISBI in an octahedral geometry. Trans-chelating phosphanes are rarely encountered[9,10] but nevertheless are of great interest in catalytic systems.[11,12]

Molecular Modeling and Conclusion. It is evident from molecular modeling (based on the structure of **1**) that BISBI is able to adopt to metals in both cis and trans positions. On the basis of a P···P′ distance of 5 Å across a P–M–P′ moiety and a P–M–P′ angle of 180°, simple molecular dynamics calculations unfold the possibility of trans-chelating BISBI (Figure 3). Only a small deformation of the ideal angle for a sp^2-hybridized carbon atom is necessary to generate this special conformation.

The bite angle of BISBI seems to decrease as the number of ligands at the metal center increases. Tetracoordinate planar nickel complexes of [Ni(BISBI)]X$_2$ type should thus provide bite angles greater than hitherto known. Tetrahedral coordination is also conceivable as it is known for diphosphanes with long flexible backbones.[13] Note: donor ligands like X = NCS$^-$ or CN$^-$ should favor the trans configuration. In other words, the BISBI ligand is conformationally flexible enough to span the entire range of 90–180° bite angles upon metal coordination. Fluctional processes including this diphos ligand should thus fully function. On the other hand, the eight-atom backbone of BISBI is still short enough that *inter*molecular coordination does *not* prevail as our report and Casey's report show.

Experimental Section

General Procedures. ^{1}H NMR spectra were measured on a JEOL JMN-GX 400 spectrometer. ^{13}C{^{1}H} NMR spectra were obtained on a JEOL JMN-GX 400 spectrometer operating at 100.5 MHz. ^{31}P{^{1}H} NMR spectra were measured at 20 °C on a JEOL JMN-GX 400 spectrometer (161.8 MHz) and referenced to external H$_3$PO$_4$ (85%). Infrared spectra were obtained on a Nicolet FT-IR spectrometer, Model 5-DX. Mass spectra were determined on a Finnigan MAT-90 instrument. Elemental analysis were performed in the Microanalytical Laboratories of our institute (M. Barth). Air-sensitive materials were manipulated under an inert atmosphere by using Schlenk techniques. Solvents were dried in the usual way. Molecular modeling was performed on a Silicon Graphics 4D/70 GTB with the INSIGHT/DISCOVER program of BIOSYM (M. Guba).

2,2′-Bis((diphenylphosphino)methyl)-1,1′-biphenyl (1) was synthesized according to ref 4. Spectroscopic data are as follows. ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 3.17$ ppm (dd, ^2J(HH) = 13 Hz, ^2J(PH) = 2 Hz, CH_aH$_b$, 2 H), 3.31 (d, ^2J(HH) = 13 Hz, CH$_a$$H_b$, 2 H), 6.95–7.36 (m, 28 H). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): $\delta = 33.7$ (d, ^1J(PC) = 17 Hz, CH$_2$), 126.0 (d, ^4J(PC) = 3 Hz, C$_4$), 127.4 (s, C$_5$), 128.57 (s, C$_{11}$ [para]), 128.67 (d, ^3J(PC) = 7, C$_{10}$ [meta]), 128.74 (d, ^3J(PC) = 7 Hz, C$_{10'}$ [meta]), 129.1 (s, C$_{11'}$ [para]), 130.0 (d, ^3J(PC) = 10 Hz, C$_3$), 130.9 (s, C$_6$), 133.0 (d, ^2J(PC) = 18.3 Hz, C$_9$ [ortho]) 133.5 (d, ^2J(PC) = 19.0 Hz, $C_{9'}$ [ortho]), 136.15 (d, ^2J(PC) = 9.2 Hz, C$_2$), 138.7 (d, ^1J(PC) = 16.8 Hz, C$_8$ [ipso]), 138.94 (d, ^1J(PC) = 16.8 Hz, C$_{8'}$ [ipso]), 141.3 (d, ^3J(PC) = 4.6 Hz, C$_1$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): $\delta = -9.8$ (s). IR (KBr, cm^{-1}): ν(aryl—H) 3067 (m), 767 (s), 741 (vs), 695 (vs), ν(C═C) 1580 (m), ν(C—H) 3051 (m), 1477 (s), ν(aryl—P) 1433 (s). MS (CI): m/e = 551.2 ([MH]$^+$), 365.1 ([MH - PPh$_2$]$^+$). Anal. Calcd for C$_{38}$H$_{32}$P$_2$: C, 82.89; H, 5.86; P, 11.25. Found: C, 82.56; H, 5.77; P, 11.10. Mp: 83 °C.

Table III. Final Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **3** with Estimated Standard Deviations in Parentheses and Starred Values Denoting Atoms That Were Refined with Isotropic Displacement Parameters

atom	x/a	y/b	z/c	B_{eq},[a] Å^2
Mo	0.43306 (2)	0.13743 (3)	0.14214 (2)	2.753 (6)
P1	0.57377 (7)	0.12706 (8)	0.22035 (6)	2.49 (2)
P2	0.32087 (7)	0.05569 (9)	0.22011 (3)	2.53 (2)
O1	0.2912 (2)	0.1689 (4)	0.0197 (2)	9.2 (1)
O2	0.5356 (2)	0.2579 (3)	0.0316 (2)	5.7 (1)
O3	0.3768 (3)	0.3374 (3)	0.2057 (2)	7.1 (1)
O4	0.4563 (3)	−0.0644 (3)	0.0662 (2)	6.5 (1)
C1	0.3400 (3)	0.1550 (4)	0.0664 (3)	5.2 (1)
C2	0.5019 (3)	0.2109 (4)	0.0725 (3)	3.8 (1)
C3	0.3989 (3)	0.2639 (4)	0.1855 (3)	4.4 (1)
C4	0.4529 (3)	0.0070 (4)	0.0953 (3)	4.0 (1)
C11	0.6719 (3)	0.1353 (3)	0.1682 (2)	2.9 (1)
C12	0.7480 (3)	0.1741 (4)	0.1985 (3)	4.0 (1)
C13	0.8227 (3)	0.1756 (4)	0.1598 (3)	5.1 (1)
C14	0.8225 (3)	0.1386 (4)	0.0905 (3)	4.8 (1)
C15	0.7477 (3)	0.0991 (4)	0.0604 (3)	4.4 (1)
C16	0.6727 (3)	0.0982 (4)	0.0984 (2)	3.5 (1)
C21	0.5909 (3)	0.2250 (3)	0.2846 (2)	3.1 (1)
C22	0.6051 (3)	0.2123 (4)	0.3590 (3)	4.6 (1)
C23	0.6190 (4)	0.2910 (4)	0.4044 (3)	5.7 (1)
C24	0.6185 (4)	0.3805 (4)	0.3781 (3)	5.6 (1)
C25	0.6047 (4)	0.3948 (4)	0.3046 (3)	6.0 (2)
C26	0.5910 (4)	0.3180 (4)	0.2590 (3)	4.8 (1)
C31	0.2171 (3)	0.0529 (3)	0.1669 (2)	2.6 (1)
C32	0.1732 (3)	0.1380 (3)	0.1546 (2)	3.5 (1)
C33	0.0965 (3)	0.1402 (4)	0.1136 (3)	4.2 (1)
C34	0.0636 (3)	0.0568 (4)	0.0834 (3)	4.8 (1)
C35	0.1061 (3)	−0.0275 (4)	0.0956 (3)	4.7 (1)
C36	0.1832 (3)	−0.0308 (3)	0.1371 (2)	3.5 (1)
C41	0.2893 (3)	0.1161 (3)	0.3031 (2)	3.1 (1)
C42	0.2061 (3)	0.1126 (4)	0.3268 (3)	4.3 (1)
C43	0.1873 (4)	0.1568 (5)	0.3918 (3)	6.0 (2)
C44	0.2516 (4)	0.2020 (4)	0.4330 (3)	6.3 (2)
C45	0.3341 (4)	0.2045 (4)	0.4104 (3)	5.6 (1)
C46	0.3539 (3)	0.1631 (4)	0.3444 (2)	4.0 (1)
C50	0.6026 (3)	0.0222 (3)	0.2780 (2)	3.2 (1)
C51	0.5862 (3)	−0.0732 (3)	0.2415 (2)	3.0 (1)
C52	0.6413 (3)	−0.1053 (4)	0.1876 (3)	4.0 (1)
C53	0.6234 (3)	−0.1888 (4)	0.1509 (3)	4.9 (1)
C54	0.5516 (4)	−0.2435 (3)	0.1661 (3)	4.9 (1)
C55	0.4997 (3)	−0.2146 (3)	0.2218 (3)	3.7 (1)
C56	0.5172 (3)	−0.1308 (12)	0.2597 (2)	2.8 (1)
C60	0.3278 (3)	−0.0718 (3)	0.2517 (2)	3.1 (1)
C61	0.3789 (3)	−0.0869 (3)	0.3220 (2)	2.8 (1)
C62	0.3358 (3)	−0.0772 (4)	0.3861 (3)	4.0 (1)
C63	0.3801 (4)	−0.0868 (4)	0.4528 (3)	4.8 (1)
C64	0.4676 (3)	−0.1058 (4)	0.4560 (3)	4.2 (1)
C65	0.5104 (3)	−0.1174 (3)	0.3930 (2)	3.5 (1)
C66	0.4667 (3)	−0.1093 (3)	0.3249 (2)	2.8 (1)
C100	0.1068 (10)	0.0115 (8)	0.5505 (8)	22.1 (6)*
Cl1	0.1845 (5)	−0.0363 (6)	0.5993 (4)	16.9 (1)*
Cl2	0.0289 (5)	0.0061 (6)	0.6106 (4)	16.9
Cl3	0.1413 (5)	−0.0818 (6)	0.5183 (4)	16.9
Cl4	0.2146 (5)	0.0662 (6)	0.6034 (4)	16.9

[a] $B_{eq} = {}^4/_3[a^2\beta(11)+b^2\beta(22)+c^2\beta(33) + ac(\cos\beta)\beta(13)]$.

[2,2′-Bis((diphenylphosphino)methyl)-1,1′-biphenyl]tetracarbonylmolybdenum (3). To a solution of (bicyclo[2.2.1]-hepta-2,5-diene)-tetracarbonylmolybdenum(0) (**2**)[14] (600 mg, 2 mmol) dissolved in 20 mL of toluene was added 1.1 g (2 mmol) of **1** in 20 mL of toluene dropwise at room temperature. The solution was then heated to reflux for 5 min and subsequently cooled to ambient temperature. The resulting solid was filtered off and dissolved in a minimum amount of methylene chloride. Yellow crystals were grown by diffusion of n-hexane into this solution at room temperature, resulting in a yield of 47% (396 mg) of **3**. Elemental analyses showed that crystals of **3** include 0.92 equiv of methylene chloride due to partial solvent loss. Spectroscopic data are as follows. ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 3.62$ ppm ("t", CH_aH$_b$, 2 H), 3.92 (d, ^2J(PH)

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Table IV. Selected Bond Lengths (Å) and Angles (deg) for 2,2′-Bis(diphenylphosphino)methyl)-1,1′-biphenyl (**1**) and [2,2′-Bis((diphenylphosphino)methyl)-1,1′-biphenyl]tetracarbonylmolybdenum (**3**)

1				3			
(A) Bond Lengths							
P(1A)–C(11A)	1.841 (5)	P(1B)–C(11B)	1.830 (5)	P(1)–C(11)	1.836 (2)	Mo–P(1)	2.561 (1)
P(1A)–C(21A)	1.837 (5)	P(1B)–C(21B)	1.832 (5)	P(1)–C(21)	1.824 (2)	Mo–P(2)	2.570 (1)
P(1A)–C(50A)	1.873 (4)	P(1B)–C(50B)	1.868 (5)	P(1)–C(50)	1.855 (2)	Mo–C(1)	1.979 (2)
P(2A)–C(31A)	1.840 (5)	P(2B)–C(31B)	1.841 (5)	P(2)–C(31)	1.844 (2)	Mo–C(2)	1.992 (2)
P(2A)–C(41A)	1.839 (4)	P(2B)–C(41B)	1.829 (5)	P(2)–C(41)	1.836 (2)	Mo–C(3)	2.019 (3)
P(2A)–C(60A)	1.869 (4)	P(2B)–C(60B)	1.863 (5)	P(2)–C(60)	1.875 (2)	Mo–C(4)	2.046 (2)
C(56A)–C(66A)	1.492 (6)	C(56B)–C(66B)	1.498 (6)	C(56)–C(66)	1.497 (3)		
(B) Bond Angles							
C(11A)–P(1A)–C(21A)	101.9 (2)	C(11B)–P(1B)–C(21B)	102.6 (2)	C(11)–P(1)–C(21)	101.3 (1)	P(1)–Mo–P(2)	103.54 (2)
C(11A)–P(1A)–C(50A)	104.4 (2)	C(11B)–P(1B)–C(50B)	101.4 (2)	C(11)–P(1)–C(50)	99.8 (1)	P(1)–Mo–C(1)	168.3 (1)
C(21A)–P(1A)–C(50A)	99.6 (2)	C(21B)–P(1B)–C(50B)	99.8 (2)	C(21)–P(1)–C(50)	101.1 (1)	P(1)–Mo–C(2)	86.0 (1)
				Mo–P(1)–C(11)	113.5 (1)	P(1)–Mo–C(3)	93.1 (1)
				Mo–P(1)–C(21)	114.9 (1)	P(1)–Mo–C(4)	92.9 (1)
				Mo–P(1)–C(50)	123.8 (1)	P(2)–Mo–C(1)	88.1 (1)
						P(2)–Mo–C(2)	169.9 (1)
C(31A)–P(2A)–C(41A)	102.2 (2)	C(31B)–P(2B)–C(41B)	103.4 (2)	C(31)–P(2)–C(41)	101.5 (1)	P(2)–Mo–C(3)	88.3 (1)
C(31A)–P(2A)–C(60A)	103.7 (2)	C(31B)–P(2B)–C(60B)	98.3 (2)	C(31)–P(2)–C(60)	100.6 (1)	P(2)–Mo–C(4)	87.7 (1)
C(41A)–P(2A)–C(60A)	98.9 (2)	C(41B)–P(2B)–C(60B)	101.7 (2)	C(41)–P(2)–C(60)	100.9 (1)	C(1)–Mo–C(2)	82.5 (1)
				Mo–P(2)–C(31)	107.8 (1)	C(1)–Mo–C(3)	88.8 (1)
				Mo–P(2)–C(41)	118.5 (1)	C(1)–Mo–C(4)	85.9 (1)
				Mo–P(2)–C(60)	124.5 (1)	C(2)–Mo–C(3)	87.9 (1)
						C(2)–Mo–C(4)	95.2 (1)
						C(3)–Mo–C(4)	173.5 (1)

= 13 Hz, CH_aH_b, 2 H), 6.16 (d, ^3J(HH) = 8 Hz, H_6, $H_{6'}$, 2 H), 6.84 (dt, ^3J(HH) = 7 Hz, ^4J(HH) = 1.2 Hz, H_5, $H_{5'}$, 2 H), 7.03 (dd, ^3J(HH) = 7 Hz, ^4J(HH) = 1.2 Hz, H_3, $H_{3'}$, 2 H), 7.16 (t, ^3J(HH) = 8 Hz, H_4, $H_{4'}$, 2 H), 7.26–7.46 (m, 20 H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 38.24 (d, ^1J(PC) = 5 Hz, C_7), 38.29 (d, ^1J(PC) = 5 Hz, $C_{7'}$), 126.71 (d, ^2J(PC) = 7 Hz, C_9 [ortho]), 127.13 (d, ^2J(PC) = 7 Hz, $C_{9'}$ [ortho]), 128.10 (d, ^3J(PC) = 4 Hz, C_{10} [meta]), 128.59 (d, ^3J(PC) = 4 Hz, C_{10}' [meta]), 128.98 ($C_{4,4'}$), 130.52 (C_5), 130.80 ($C_{5'}$), 130.90 (C_6), 131.38 ($C_{6'}$), 133.22 (s, $C_{11,11'}$ [para]), 135.66 (C_3), 135.71 ($C_{3'}$), 136.31 ("qui"; N = 30.5 Hz, $C_{2,2'}$), 141.94 (s, $C_{1,1'}$), 142.75 ("qui", N = 34.1 Hz, $C_{8,8'}$ [ipso]), 208.64 (t, ^2J(PC) = 9.8 Hz, CO [trans]), 214.81 ("qui", N = 18.3 Hz, CO [cis]). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 31.49 (s). IR (KBr, cm^{-1}, ν(CO)): 2021 (s), 1926 (vs), 1900 (vs), 1879 (vs). MS (EI, 70 eV): m/e = 648 ($[M - 4CO]^{\bullet+}$), 551 ($[BISBI]^{\bullet+}$). MS (CI): m/e = 758 ($[M]^+$), 646 ($[M - 4CO]^{\bullet+}$). Anal. Calcd. for $C_{43}H_{34}Cl_2MoO_4P_2$: C, 61.23; H, 4.06; O, 7.59; Cl, 8.41; P, 7.34; Mo, 11.37. Found: C, 61.11; H, 4.24; O, 7.80; Cl, 7.89; P, 7.40; Mo, 11.70. Mp: 83 °C dec.

X-ray Crystallography. Crystals of compounds **1** and **3** were grown by standard techniques at room temperature from an ethanol solution and a methylene chloride/hexane mixture, respectively. Preliminary examination and data collection were carried out with Cu Kα radiation on an Enraf-Nonius CAD4 diffractometer. Final cell constants were obtained by least-squares analysis of 25 automatically centered reflections (80° < 2θ < 88° and 81° < 2θ < 95°, respectively). Data were collected by a $\theta/2\theta$ scan mode, orientation control reflections were monitored every 200th, and the intensities of three reflections were checked every 3600 s. Changes in intensities for **3** were corrected. Crystal data and intensity collection parameters together with details of the refinements are summarized in Table I.

Both structures were solved by direct methods and subsequent difference Fourier maps. Full-matrix least-squares refinement was carried out by minimizing $\sum w(|F_o| - |F_c|)^2$. Final positional parameters are given in Tables II and III; selected bond angles and distances are given in Table IV. Hydrogen atoms were included at their calculated positions (d_{C-H} = 95 pm) for compound **3**. For compound **1**, all hydrogen atoms could be located in Fourier maps. In both cases the hydrogen atoms were not refined. Anomalous dispersion is considered. The refinements stopped at shift/error < 0.001, and final difference Fourier maps showed no significant features. All calculations were performed on VAX 11/730 and MicroVAX 3100 computers with the STRUX-III system[15] including the programs MULTAN, SIR88, ORTEP, PLATON, SCHAKAL, SDP, SHELX-76 (extended version for 1000 parameters), and SHELX-86.

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Registry No. **1**, 136379-28-7; **2**, 12146-37-1; **3**, 136391-51-0.

Supplementary Material Available: For both structures, a complete table of crystallographic data and tables of atom positions, anisotropic displacement parameters, and bond distances and angles for all atoms (37 pages); listings of calculated and observed structure factors for both structures (67 pages). Ordering information is given on any current masthead page.

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