Transition-Metal Complexes Containing *trans*-Spanning Diphosphine Ligands

Carol A. Bessel* and Pooja Aggarwal

Department of Chemistry, Villanova University, Villanova, Pennsylvania 19085

Amy C. Marschilok and Kenneth J. Takeuchi*

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14260

Received November 2, 2000 (Revised Manuscript Received February 1, 2001)

Contents

I. Introduction

To better understand four- and six-coordinate geometries around transition-metal centers, Werner systematically prepared transition-metal complexes which contained mono- and bidentate ligands.[1] Through analogy with five-membered organic rings, Werner postulated that a chelating ligand such as 1,2-diaminoethane would attach itself to a single metal center only at *cis*-positions.[2] By eliminating a *trans*-spanning geometry as a possibility for chelating ligands that form five-membered rings (including the metal center), Werner used the number of isomers available to a particular complex to correctly assign the coordination geometry about the metal center of interest.

Long after Werner's pioneering work with chelating ligands, a *trans*-spanning bidentate ligand remained an intriguing synthetic problem. While the possibility of synthesizing complexes in which a bidentate ligand spans across the metal center at an angle of 180° was clearly recognized, early efforts to synthesize such complexes failed or lead to questionable success.[3] It was not until 1961, when Issleib and Hohlfeld prepared a square planar nickel complex using the simple bidentate diphosphine ligand, $(C_6H_{11})_2P(CH_2)_5P(C_6H_{11})_2$ (Figure 1), that it was generally accepted that the preparation of transition-metal complexes containing *trans*-spanning bidentate ligands could be accomplished.[4]

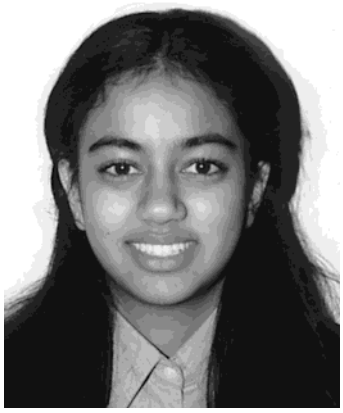
This article represents the first review of the Issleib and Hohlfeld report and subsequent research efforts (ca. 1960−2000) in which the objective of spanning the *trans*-positions of a transition-metal center with a bidentate diphosphine ligand was achieved. In light of the excellent reviews that exist on the formation of many-membered ring chelate complexes,[5−9] we have limited our review to *trans*-spanning diphosphine ligands and their transition-metal complexes. These ligands contain two phosphorus donor atoms coordinated to the metal center. Notably, we have omitted complexes in which the P−metal−P angle is large (i.e., 90−130°)[10−13] but does not approach 180°. Also, diphosphine ligands which contribute other donor atoms in terdentate or multidentate fashion (e.g., C (cyclometalation),[14−16] O,[10,17] N, metal,[11] or other atoms) may be mentioned in comparison to complexes that contain *trans*-spanning diphosphine ligands but are not a specific topic of this review.

Tables have been used to summarize the physical data for the *trans*-spanning phosphine ligands (Tables 1−5).

Since the formation of transition-metal complexes that contain a *trans*-spanning bidendate phosphine ligand remains an important synthetic challenge, we have partitioned this review into two general categories, according to the two general methods of preparation currently in use. The first method of synthesizing transition-metal complexes which contain *trans*-spanning bidentate phosphine ligands involves the initial synthesis of the bidentate phosphine ligand

10.1021/cr990346w CCC: $36.00
Published on Web 03/15/2001

Carol A. Bessel was born in Buffalo, NY, in 1966. She graduated with both her B.S. (1988) and Ph.D. (1993) degrees in Chemistry at the State University of New York at Buffalo. In 1993, she received a National Research Council/Naval Research Laboratory Postdoctoral Fellowship. Since 1995, she has been an Assistant Professor of Chemistry at Villanova University. Her recent honors include a Bunting Fellowship at the Radcliffe Institute of Advanced Studies at Harvard University (1999–2000). Her present research interests include ruthenium coordination chemistry, supercritical fluid catalysis, and the synthesis and characterization of novel solid-state materials.



Pooja Aggarwal was born in Flushing, NY, in 1979. She is currently a senior Chemistry major at Villanova University, where she will earn her Bachelor of Science degree in 2001. Her research lies in the area of ruthenium coordination chemistry.

and the subsequent coordination of the bidentate phosphine ligand to the transition-metal center (hereafter referred to as the preformed ligand strategy). The second method involves bonding two monodentate ligands to the metal center and then joining the ligands with a *trans*-spanning linkage (hereafter referred to as the in situ ligand strategy).

II. Preformed Ligand Strategy

A. Preformed Linear and Trigonal Complexes

Venanzi and co-workers extensively researched the ligand 2,11-bis(diphenylphosphinomethyl)benzo[*c*]-phenanthrene (L1a) which because of its size and rigidity was initially believed to be able to form *cis*-chelate rings.[18−21] The L1a ligand has been used as a *trans*-spanning "spacer" to bridge distorted trigonal, pseudo-tetrahedral, square planar, square pyramidal, and octahedral metal centers. We describe its use in linear and trigonal complexes in this section. Three-coordinate complexes of the type [MCl(L1a)], where

Amy C. Marschilok was born in Longbranch, NJ, in 1978. She graduated *magna cum laude* with her B.A. degree in Chemistry (English minor) at the State University of New York at Buffalo (1999), and she is currently in the graduate program in the Department of Chemistry at the State University of New York at Buffalo. Her research projects include the synthesis and characterization of novel solid materials, the study of novel materials in battery applications, and the preparation of coordination complexes that use unusual ligands.

Kenneth J. Takeuchi was born in Cincinnati, OH, in 1953. He received his B.S. degree *(summa cum laude)* in Chemistry from the University of Cincinnati (1975) and his Ph.D. degree in Chemistry from the Ohio State University (1981). After a postdoctoral research experience at the University of North Carolina at Chapel Hill (1981–1983), he accepted an Assistant Professor position in the Department of Chemistry at the State University of New York at Buffalo, with subsequent promotions to Associate Professor (1990) and Professor (1998). As a faculty member at the State University of New York at Buffalo, he received three Student Association Teaching Awards (1984, 1989, 1997), a Chancellor's Award for Excellence in Teaching (1986), the Dean of Natural Sciences and Mathematics award for Excellence in Teaching (1997), a Friend of EOP Award (1993), honorary memberships in Phi Eta Sigma (1986), Mortar Board (1994), and Golden Key (1997), and a national CMA Catalyst Award (1997). He has coauthored approximately 60 publications in refereed journals and over 100 presentations at scientific meetings. His current research interests include coordination chemistry, novel ligand design, solid-state materials preparation, and battery chemistry.

M = Cu(I), Ag(I), and Au(I), have been synthesized and characterized by NMR spectroscopy and crystal structure determinations (Figure 2).[22] Analysis of the X-ray crystal structures of these complexes demonstrated dramatic differences in their coordination geometries. The P(1)−M−P(2) bond angles increase down the series, 132° (Cu) < 141° (Ag) ≪ 176° (Au), and as the P(1)−M−P(2) bond angles open, the M−P bond lengths shorten and strengthen whereas the M−Cl bonds lengthen and weaken.[22] These changes in P(1)−M−P(2) bond angles indicate that while the

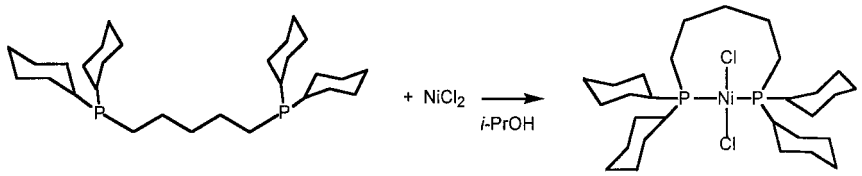


Figure 1. Preparation of *trans*-[Ni{$(C_6H_{11})_2P(CH_2)_5P(C_6H_{11})_2$}$Cl_2$], the first example of a *trans*-spanning diphosphine complex.[4]

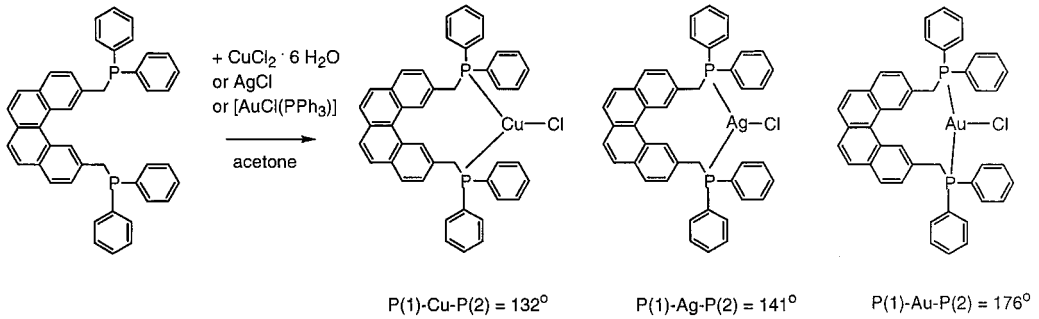


Figure 2. Preparations of three-coordinate, *trans*-spanning complexes using the L1a ligand.[22]

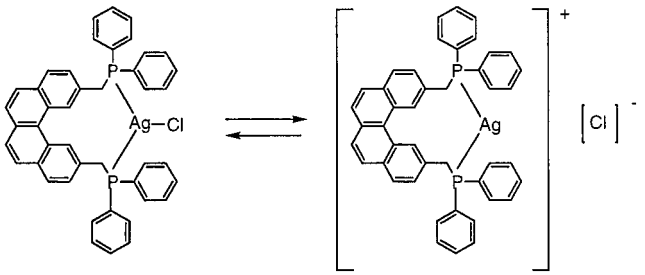


Figure 3. Solution-phase ionization equilibrium of [Ag(L1a)Cl].[23]

L1a ligand can adopt a nearly trigonal planar coordination geometry, its steric requirements prefer linear P(1)−M−P(2) bonds.[22]

While complexes of copper(I), silver(I), and gold(I) seem relatively simple due to their preference for low coordination numbers, the chemistries of such complexes are often complicated by the competition between ionic and covalent ligand coordination, the ability of the complexes to undergo ligand exchange, and the possibility of anionic ligands bridging metal centers. Complexes containing varying anions, [M(L1a)X], where M = Cu(I), Ag(I), or Au(I) and X = I^-, Cl^-, NO_3^-, or BF_4^-, were compared on the basis of their molecular weight, conductivity, and NMR spectra. While all the complexes were associated in CH_2Cl_2, the nitrate- and tetrafluoroborate-containing complexes existed as ionic species ($[M(L1a)]^+$ X^-) when dissolved in CH_3CN or CH_3NO_2 and the halide-containing complexes existed as equilibrium mixtures of "covalent" ([M(L1a)X]) and "ionic" ($[M(L1a)]^+$ X^-) species in CH_3CN or CH_3NO_2 (Figure 3).[23] As demonstrated in the solid-state structures, the widening of the P(1)−M−P(2) bond angle marked an increase in the ionic character of the M−Cl bond. It was observed that the gold halide complexes are generally more ionic than their copper and silver analogues. This is consistent with the greater tendency of gold(I) toward two-coordinate complexes than copper(I) or silver(I).

The competition between ionic and covalent ligand coordination in the silver(I) complexes was further elucidated by NMR studies of [Ag(L1a)Cl] and [Ag(L1a)]BF_4. In these studies, $^1J(^{107}Ag-^{31}P)$ coupling constants were used to determine the coordination number of the silver ion in solution. The ^1J values of [Ag(L1a)Cl] and [Ag(L1a)]BF_4 are 411 and 515 Hz, respectively, indicating that in CD_2Cl_2 the former is a three-coordinate species while the latter is a two-coordinate species, ion-paired to the BF_4^- anion. The δ ^{31}P values of 6.25 and 12.06 ppm, respectively, also reflect the decrease in coordination number.[23] In acetonitrile, these two silver complexes can form $[Ag(CH_3CN)_n(L1a)]^+$, where n is probably equal to 2, thereby demonstrating the complicated ligand exchange reactions that are possible with Cu(I), Ag(I), and Au(I) metal centers.[23]

The X-ray crystal structures of [Ag(L1a)X], where X = Cl^-, $SnCl_3^-$ (bound via Cl), NO_3^-, and ClO_4^-, have also been reported.[24] The Ag atom in [Ag(L1a)Cl] shows a distorted trigonal coordination, while the other complexes are formally four-coordinate with slightly different Ag−Cl or Ag−O bonds to the chelating anions. The P(1)−Ag−P(2) angle increases Cl^- (140.7(1)°) < $SnCl_3^-$ (142.2(1)°) < NO_3^- (148.6(1)°) < ClO_4^- (151.5(1)°), and the M−P bonds are generally unequal (differing by 0.043 Å for Cl^-, 0.032 Å for $SnCl_3^-$, and 0.16 Å for ClO_4^-). These differences may be indicative of the close contacts between the anion, the *ipso* position of the phenyl groups attached to the phosphine, and the C(1) position of the L1a ligand. The M−anion bonds are generally longer than M−P bonds in the above [Ag(L1a)X] complexes, indicating that the anion has a partially ionic character, as described above.[24] Notably, the L1a ligand conformations for complexes containing Cl^-, NO_3^-, and ClO_4^- were different than that for $SnCl_3^-$. This change in ligand conformation modified the author's previous ideas about P(1)−Ag−P(2) bond angles influencing the conformation of the L1a ligand (vide infra).

A further series of three-coordinate silver(I) complexes with L1b or L1e (see Figure 4 for ligand abbreviations) and anion = BF_4^-, ClO_4^-, NO_3^-, Cl^-, Br^-, or I^- were prepared and characterized by ^{31}P

Table 1. ^{31}P NMR Data for Diphosphine Transition-Metal Complexes and Uncoordinated Diphosphine Ligands

complex name	δ (^1J(M−^{31}P))[a] ppm (Hz)	ref
transition-metal complexes		
[Cu(L1a)I]	−4.66[b,c]	23
[Cu(L1a)Cl]	−4.54[b,c]	23
[Cu(L1a)(NO_3)]	−4.50[b,c]	23
[Fe($CO)_3$($PPh_3)_2$]	82.3[d,e]	83
[Fe($Ph_2PCH_2Ph)_2$($CO)_3$]	81.6[d,f]	83
[Fe(L1a)($CO)_3$]	76.1[d,f]	83
[Au(L1a)I]	38.07[d]	23
[Au(L1a)Cl]	40.91[d]	23
[Au(L1a)(NO_3)]	42.98[d]	23
trans-[Au((3-$C_6H_4PPh_2)_2$-α-cyclodextrin)]	15.4[d]	30
trans-[Au(L^1)]BF_4	36.9[d]	28
trans-[Ir(L1a)(CO)I]	14.51[d]	53
trans-[Ir(L1a)(CO)Br]	18.98[d]	53
trans-[Ir(dpd)(CO)Br]	21.0[d]	42
trans-[Ir($Ph_2PCH_2Ph)_2$(CO)Cl]	23.08[d]	53
trans-[Ir(L1a)(CO)Cl]	21.7[f,g]	101
trans-[Ir(L1a)(CO)Cl]	21.72[d]	53
trans-[Ir(dpd)(CO)Cl]	26.3[d]	42
trans-[Ir(L1a)(CO)(NCS)]	21.23[d]	53
trans-[Ir(CH_3CN)($Ph_2PCH_2Ph)_2$(CO)][BF_4]	21.75[d]	53
trans-[Ir(CH_3CN)(L1a)(CO)][BF_4]	22.08[d]	53
[Ir(L1a)(CO)HI_2]	−21.07[d]	53
[Ir(L1a)Br_2(CO)H]	−5.37[d]	53
[Ir(L1a)(CO)Cl_2H]	6.47[d]	53
[Ir($Ph_2PCH_2Ph)_2$(CO)Cl_2H]	−0.76[d]	53
[Ir($Ph_2PCH_2Ph)_2$($CO)_2H_2$][BF_4]	2.05[d]	53
[Ir(L1a)($CO)_2H_2$][BF_4]	−3.22[d]	53
trans-[Ir(L1a)(CO)H_2I]	0.10[d]	53
[Ir(CH_3CN)(L1a)(CO)H_2][BF_4]	4.46[d]	53
[Ir(CO)Cl(crown-P_2)]	10.6[d]	51
[Ir{CH_3CO_2Pb(crown-P_2)}(CO)Cl][CH_3CO_2]	22.7[d]	51
[Ir(CO)Cl{ClPb(crown-P_2)}][BPh_4]	23.0[h]	51
[Ir(CO)Cl{ClPb(crown-P_2)}]Cl	22.9[d]	51
[Ir(CO)Cl{Pb(crown-P_2)}][$BPh_4]_2$	23.7[h]	51
[Ir(CO)Cl{ClSn(crown-P_2)}]($SnCl_3$)	25.3[d]	51
[Ir(CO)Cl{Na(crown-P_2)}][BPh_4]	19.0[d]	51
[Ir(CO)I{Na(crown-P_2)}]I	15.7[d]	51
[Ir(CO)Br{Na(crown-P_2)}]Br	17.6[d]	51
[Ir(CO)I{K(crown-P_2)}]I	11.4[d]	51
[Ir(CO)Cl{K(crown-P_2)}][PF_6]	15.7[d]	51
trans-[Mo{$Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$}($CO)_4$]	32.57[f]	90
trans-[Mo{$Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$}($CO)_4$]	32.54[f]	89
trans-[Mo{1,2-($Ph_2P(CH_2CH_2O)_2)_2C_6H_4$}($CO)_4$]	34.23[f]	90
cis-[Mo{1,2-($Ph_2P(CH_2CH_2O)_2)_2C_6H_4$}($CO)_4$]	20.41[f]	90
trans-[Ni(pop)I_2]	29.31[d]	27
trans-[Ni(pop)Br_2]	14.03[d]	27
trans-[Ni(pop)Cl_2]	6.9[d]	62
trans-[Ni(pop)Cl_2]	6.51[d]	27
trans-[Ni(L1a)Cl_2]	6.5[i]	57
trans-[Ni(L1d)Cl_2]	8.30[i]	57
trans-[Ni(L1e)Cl_2]	9.45[i]	57
trans-[Ni(L1f)Cl_2]	6.76[i]	57
trans-[Ni(L1g)Cl_2]	4.16[c]	57
trans-[Ni(L1a)($NCS)_2$]	14.9[f,g]	101
trans-[Ni(L1b)($NCS)_2$]	41.06[i]	57
trans-[Ni(L1d)($NCS)_2$]	14.36[i]	57
trans-[Ni(L1e)($NCS)_2$]	27.41[i]	57
trans-[Ni(L1f)($NCS)_2$]	14.92[i]	57
trans-[Ni(L1g)($NCS)_2$]	13.53[i]	57
trans-[Ni(pop)($NCS)_2$]	12.6[d]	62
trans-[Ni(pop)($NCS)_2$]	12.83[d]	27
trans-[Ni(pop)($CN)_2$]	24.85[d]	27
trans-[Pd{$Ph_2P(CH_2)_{12}PPh_2$}I_2]	−7.00[d]	43
trans-[Pd(pop)I_2]	7.24[d]	27
trans-[Pd(dpdo)I_2]	−6.5[d]	62
trans-[Pd(pop)Br_2]	17.17[d]	26
trans-[Pd(dpdo)Br_2]	−14.5[d]	72
trans-[Pd{$Ph_2P(CH_2)_{12}PPh_2$}Cl_2]	−16.58[d]	43
trans-[Pd{$Ph_2P(CH_2)_{12}PPh_2$}Cl_2]	17.42[d]	74
trans-[Pd{$Ph_2P(CH_2CH_2O)_3CH_2CH_2PPh_2$}$Cl_2$]	14.77[d]	74
trans-[Pd{$Ph_2P(CH_2CH_2O)_5CH_2CH_2PPh_2$}$Cl_2$]	13.56[d]	74

Table 1 (Continued)

complex name	δ (^1J(M−^{31}P))[a] ppm (Hz)	ref
trans-[Pd{$Ph_2P(o\text{-}C_6H_4)NHC(O)$(2,6-pyridine)-$C(O)NH(o\text{-}C_6H_4)PPh_2$}$Cl_2$]	19.4[d,j]	80
trans-[Pd(pop)Cl_2]	20.10[d]	27
trans-[Pd(L1a)Cl_2]	19.7[f,g]	101
trans-[Pd(L1b)Cl_2]	42.15[i]	57
trans-[Pd(L1d)Cl_2]	21.40[i]	57
trans-[Pd(L1e)Cl_2]	26.75[i]	57
trans-[Pd(L1f)Cl_2]	19.62[i]	57
trans-[Pd(L1 g)Cl_2]	17.60[i]	57
trans-[Pd(pop)Cl_2]	19.6[d]	62
trans-[Pd(dpdo)$(NCS)_2$]	−13.8[d]	72
trans-[Pd(pop)$(NO_3)_2$]	14.23[d]	27
trans-[Pd$(N_3)_2$(pop)]	19.10[d]	27
trans-[Pd(L1a)Me_2]	21.3[d]	60
trans-[$PdCl_2${Y(O)}]	13.0 (−[y])[f,x]	81
trans-[$CaPdCl_2${Y(O)}]	18.3(−[y])[f,x]	81
trans-[Pd{(3-$C_6H_4PPh_2)_2$-α-cyclodextrin}]	24.5[d]	30
cis-[Pd{(3-$C_6H_4PPh_2)_2$-α-cyclodextrin}]	33.5[d]	30
trans-[Pd{$(Ph_2P)_2$-substituted calix[4]arene}-(CH_3)(pyridine)]BF_4	27.0[d]	20
trans-[Pt(L1a)I_2]	4.1 (2429)[d]	50
trans-[Pt(pop)I_2]	4.74 (2451)[d]	27
trans-[Pt(dpdo)I_2]·KCl	0.9 (2411)[d]	72
trans-[Pt(L1a)Br_2]	12.6 (2492)[d]	50
trans-[Pt(pop)Br_2]	13.09 (2521)[d]	27
trans-[Pt$(PPh_3)_2Cl_2$]	20.1 (2637)[d,g]	56
trans-[Pt(L1a)Cl_2]	16.8 (2602)[d]	50
trans-[Pt(L1a)Cl_2]	16.7 (2581)[d,g]	56
trans-[Pt(L1a)Cl_2]	18.6 (2602)[f,g]	101
trans-[Pt(L1b)Cl_2]	29.51 (2419)[f]	57
trans-[Pt(L1d)Cl_2]	18.58 (2640)[f]	57
trans-[Pt(L1e)Cl_2]	18.93 (2416)[f]	57
trans-[Pt(L1f)Cl_2]	16.45 (2577)[f]	57
trans-[Pt(L1g)Cl_2]	14.66 (2552)[f]	57
trans-[Pt(pop)Cl_2]	16.5 (2610)[d]	61
trans-[Pt(dpe)Cl_2]	−47.3 (2359)[d]	41
trans-[Pt(dphp)Cl_2]	−17.5 (2544)[d]	41
trans-[Pt(dpn)Cl_2]	−15.9 (2595)[d]	41
trans-[Pt(dpu)Cl_2]	−14.2 (2585)[d]	41
trans-[Pt(dph)Cl_2]	−12.4 (2548)[d]	41
trans-[Pt(dpo)Cl_2]	−16.0 (2587)[d]	41
trans-[Pt(dpd)Cl_2]	−15.5 (2595)[d]	41
trans-[Pt(dpdod)Cl_2]	−13.5 (2579)[d]	41
trans-[Pt(dpdo)Cl_2]	−14.8 (2660)[d]	72
trans-[Pt{$Ph_2P(o\text{-}C_6H_4)NHC(O)$(2,6-pyridine)-$C(O)NH(o\text{-}C_6H_4)PPh_2$}$Cl_2$]	15.4 (2457)[d,j]	80
trans-[Pt(pop)Cl_2]	15.8 (2580)[d]	62
trans-[Pt(pop)Cl_2]	16.45 (2605)[d]	27
cis-[Pt$(Ph_2PCH_2Ph)_2Cl_2$]	9.7 (3733)[d]	50
trans-[Pt$(Ph_2PCH_2Ph)_2Cl_2$]	15.6 (2585)[d]	50
trans-[Pt(*t*-$Bu_2P(CH_2)_{12}P$*t*-$Bu_2)Cl_2]_3$	27.2 (2449)[d]	33
trans-[Pt{*t*-$Bu_2P(CH_2)_{12}P$*t*-Bu_2}$Cl_2]_2$	27.2 (2450)[d]	33
trans-[Pt{*t*-$Bu_2P(CH_2)_{12}P$*t*-Bu_2}Cl_2]	28.2 (2444)[d]	33
trans-[$PtCl_2${*t*-$Bu_2P(CH_2)_{10}P$*t*-Bu_2}$Cl_2]_2$	29.5 (2451)[d]	33
trans-[$PtCl_2${*t*-$Bu_2P(CH_2)_{10}P$*t*-Bu_2}Cl_2]	31.8 (2476)[d]	33
trans-[$PtCl_2${*t*-$Bu_2P(CH_2)_9P$*t*-Bu_2}$Cl_2]_2$	28.8 (2451)[d]	33
trans-[$PtCl_2${*t*-$Bu_2P(CH_2)_9P$*t*-Bu_2}Cl_2]	31.0 (2454)[d]	33
trans-[Pt(pop)BrH]	25.16 (2975)[d]	27
trans-[Pt{$P(CH_2Ph)(p\text{-}PhCF_3)_2$}$_2$ClH]	27.4 (3072)[d,g]	58
trans-[Pt(L1a)ClH]	26.2 (2990)[d]	59
trans-[Pt(L1b)ClH]	59.06 (2836)[f]	57
trans-[Pt(L1d)ClH]	34.5 (3075)[i]	59
trans-[Pt(L1d)ClH]	27.3 (3053)[d]	58
trans-[Pt(L1e)ClH]	34.88 (2781)[f]	57
trans-[Pt(pop)ClH]	25.3 (2508)[d]	62
trans-[Pt(pop)ClH]	25.55 (2969)[d]	27
trans-[Pt(L1d)H(4-PADA)][BF_4]	28.2 (2950)[e,f]	58
trans-[Pt(L1d)(OCHO)H]	27.7 (3155)[i]	59
[Pt{*t*-$Bu_2PCH_2CH_2CMeCH_2CH_2P$*t*-$Bu_2$}H]	76.5 (3095)[d,k]	40
trans-[Pt(L1a)IMe]	19.1 (3014)[d]	27
trans-[Pt{$P(CH_2Ph)(p\text{-}PhCF_3)_2$}$_2$ClMe]	25.8 (3165)[d,g]	58
trans-[Pt(L1d)ClMe]	25.0 (3168)[d,g]	58
trans-[Pt(L1d)ClMe]	30.8 (3155)[i]	59

Table 1 (Continued)

complex name	δ (^1J(M−^{31}P))[a] ppm (Hz)	ref
trans-[Pt(L1d)Me(4-PADA)][BF_4]	22.9 (3049)[e,g]	58
trans-[Pt(L1d)Me(OMe)]	26.66 (3340)[i]	59
trans-[Pt(L1d)(CO_2H)Me]	27.0 (3258)[i]	59
trans-[Pt(L1d)(CO)Me][BF_4]	16.9 (2647)[e]	59
trans-[Pt(L1d)(CO_2H)Me]	24.5 (3131)[e]	59
trans-[Pt(L1d)(CO_2H)Me]	24.6 (3149)[i]	59
trans-[Pt(L1d)(OH)Me]	28.0 (3256)[i]	59
trans-[Pt(L1d)Me(4-PADA)][BF_4]	21.1 (3012)[e]	58
trans-[Pt(L1a)(C_2H_4)]	24.9 (3374)[l]	26
trans-[Pt(L1a)(PhC≡CMe)]	17.0 (3515)[d]	26
trans-[Pt(L1a)(PhC≡CPh)]	16.9 (3511)[d]	26
trans-[Pt(L1a)(PPh_3)]	39.8/48.7[m] (4506/4465[m])[n]	26
trans-[Pt(L1a)(O_2)]	8.4 (4099)[l]	26
trans-[Pt(L1a)(CH_2═$CHCO_2$Me)]	24.2/19.9 (4181/3532)[d,o]	26
trans-[Pt(L1a)(MeO_2CC≡CCO_2Me)]	15.5 (3692)[d]	26
trans-[Pt(L1a)(CO)]	−4.0 (3347)[p,d]	26
trans-[Pt(L1a)(O_2CMe_2*O*)]	2.3/0.9 (3491/3355)[d]	26
trans-[Pt(L1a){(*i*-Pr)O_2CC≡CCO_2(*i*-Pr)}(L1a)]	15.4 (3684)[i]	26
trans-[Pt(CH_2Ph)(L1a)Br]	16.3 (3208)[q]	26
[Pt{*t*-$Bu_2PCH_2CH_2CMeCH_2CH_2P$*t*-$Bu_2$}Cl]	73.3 (3223)[d,k]	40
[Pt{*t*-$Bu_2PCH_2CH_2CMeCH_2CH_2P$*t*-$Bu_2$}-($O_2CCF_3$)]	86.4 (3296)[d,k]	40
cis-[$PtCl_2${Y(O)}]	4.5 (3622)[f,x]	81
trans-[Pt{(Ph_2P)$_2$-substituted calix[4]arene}-$HPPh_3$]BF_4	15.0 (2706)[d]	29
trans-[Pt((3-$C_6H_4PPh_2$)$_2$-α-cyclodextrin)]	21.4 (2642)[d]	30
cis-[Pt((3-$C_6H_4PPh_2$)$_2$-α-cyclodextrin)]	15.3 (3669)[d]	30
trans-[Pt((4-$C_6H_4PPh_2$)$_2$-α-cyclodextrin)]	19.1 (2633)[d]	30
cis-[Pt((4-$C_6H_4PPh_2$)$_2$-α-cyclodextrin)]	13.4 (3681)[d]	30
trans-[PtClH(L^1)]BF_4	22.7 (3122)[d]	28
trans-[PtH(L^1)(PPh_3)]BF_4	20 (2020)[m], 14.48 (2879) (L^1)[d]	28
trans-[PtH(L^1-with coordinated amide carbonyl)]BF_4	24.8 (3166)[d]	28
trans-[PtH(L^1-with coordinated amide carbonyl)(dmad)]BF_4	16.4 (3166)[d]	28
trans-[PtH(L^1)(tcne)]BF_4	11.9 (3621)[d]	28
trans-[{PtH(L^1)}$_2$(*μ*-4,4′-bipyridine)]BF_4	22.3 (3072)[d]	28
trans-[{PtClH(L^2)}]BF_4	23.8 (3148)[d]	28
trans-[PtH(L^3)(PPh_3)]BF_4	22.7 (2006)[m], 15.9 (2879)[d] (L^3)[d]	28
trans-[PtH(L^4)(PPh_3)]BF_4	22.0 (2009)[m], 15.6 (2843)[d] (L^4)[d]	28
trans-[Rh(L1a)(CO)I]	22.86 (122)[d]	53
trans-[Rh(L1a)(CO)Br]	25.98(123)[d]	53
trans-[Rh(dpd)(CO)Br]	26.0 (109.8)[d]	42
trans-[Rh(Ph_2PCH_2Ph)$_2$(CO)Cl]	29.48(118)[d]	53
trans-[Rh(L1a)(CO)Cl]	28.16 (124)[d]	53/101
trans-[Rh(pop)(CO)Cl]	26.42 (126)[d]	27
trans-[Rh(CO)Cl(dpd)]	27.1 (111.0)[d]	42
trans-[Rh(CO)Cl(dphd)]	28.1 (112.8)[d]	42
[Rh(bdpbz)Cl(CO)]	27.7, 25.7 (127)[l]	45
trans-[Rh(CH_3CN)(L1a)(CO)][BF_4]	27.98 (120)[i]	53
trans-[Rh(L1a)(CO)(NCS)]	28.01(125)[d]	53
[Rh(bdpbz)($CO)_2$][BF_4]	27.1 (107)[l]	45
trans-[Rh(CO)Cl{(3-$C_6H_4PPh_2$)$_2$-α-cyclodextrin}]	29.7 (127.1)[d]	30
trans-[Rh(CO)(L^1-with coordinated amide carbonyl)]BF_4	18.1 (127)[d]	28
trans-[Rh(CO)(L^3-with coordinated amide carbonyl)]BF_4	20.70 (132),[d] 14.26 (132)[d]	28
[Ru($CO)_3$($PPh_3)_2$]	55.4[l]	83
[Ru($CO)_3$($Ph_2PCH_2Ph)_2$]	54.2[i,g]	83
[Ru(L1a)($CO)_3$]	49.5[d,g]	83
[Ru($Ph_2PCH_2Ph)_2$(CO)Cl(NO)]	35.1[i]	86
[Ru(CO)Cl(NO)($PPh_3)_2$]	33.7[i]	86
[Ru(L1a)(CO)Cl(NO)]	36.7[i]	86
[Ru($Ph_2PCH_2Ph)_2$Cl(NO)]	33.1[i]	86
[Ru($PPh_3)_2$Cl(NO)]	31.8[i]	86
[Ru(L1a)Cl(NO)]	31.5[i]	86
[Ru{P($OCH_2)_3$−CC_2H_5}(L1a)Cl(NO)]	36.3 (d),142.2 (t)[i,r]	86
trans-[Ru(L1a)Cl($NO)_2$][BF_4]	32.3[f,g]	87
cis,*cis*,*trans*-[Ru{*μ*-$Ph_2P(CH_2CH_2O)_4CH_2CH_2$-$PPh_2$}($CO)_2Cl_2$]	13.43[f]	91

Table 1 (Continued)

complex name	δ (^1J(M−^{31}P))[a] ppm (Hz)	ref
cis,cis,trans-[Ru{$Ph_2P(CH_2CH_2O)_5CH_2CH_2$-$PPh_2$}$(CO)_2Cl_2$]	11.16[f]	91
cis,cis,trans-[Ru{$Ph_2P(CH_2CH_2O)_4CH_2CH_2$-$PPh_2$}$(CO)_2Cl_2$]	9.74[f]	90/91
cis,cis,trans-[Ru{1,2-$(Ph_2P(CH_2CH_2O)_2)_2$-C_6H_4}$(CO)_2Cl_2$]	9.05[f]	90
cis,cis,trans-[Ru$(CO)_2Cl_2${$(Ph_2P)_2$-substituted calix[4]arene}]	12.9[d]	29
trans,trans,trans-[Ru$(CO)_2Cl_2${$(Ph_2P)_2$-substituted calix[4]arene}]	42.4[d]	29
[Ag(L1a)I]	2.57 (378,[s] 437[t])[d,g,u]	24
[Ag(L1a)I]	7.1 (408[s])[f,g]	25a
[Ag(L1b)I]	53.1 (418[s])[f,g]	25b
[Ag(L1b)I]	50.0 (391[s])[d]	27
[Ag(L1c)I]	5.2 (416[s])[f,g]	25b
[Ag(L1e)I]	20.6 (391[s])[d]	25a
[Ag(L1a)Br]	6.4 (405[s])[f,g]	25
[Ag(L1b)Br]	52.0 (412[s])[d]	25
[Ag(L1c)Br]	5.5 (435[s])[f,g]	25b
[Ag(L1e)Br]	23.4 (404[s])[d]	25a,b
[Ag(L1a)Cl]	6.25 (411,[s] 474[t])[d,g,u]	23
[Ag(L1a)Cl]	6.82 (426,[s] 493[t])[d,g,v]	23
[Ag(L1a)Cl]	7.1 (408[s])[d]	25a
[Ag(L1a)Cl]	2.6 (378[s])[f,g]	25b
[Ag(L1b)Cl]	50.0 (391[s])[f,g]	25b
[Ag(L1b)Cl]	53.1 (418[s])[f,g]	25
[Ag(L1c)Cl]	6.7 (447[s])[f,g]	25b
[Ag(L1e)Cl]	23.4 (413[s])[d]	25a
trans-[Ag(pop)Cl]·0.5acetone·0.5benzene	≈13. (420[s])[i]	27
[Ag(L1a)(BF_4)]	12.06 (515,[s] 593[t])[d,g]	23
[Ag(L1a)(BF_4)]	12.01 (510,[s] 589[t])[d,g]	23
[Ag(L1a)(BF_4)]	7.99 (466,[s] 537[t])[d,g]	23
[Ag(L1b)(BF_4)]	59.2 (453[s])[d]	25
[Ag(L1c)(BF_4)]	12.3 (511[s])[f,g]	25b
[Ag(L1c)(BF_4)]	10.2 (494[s])[f,g]	25b
[Ag(L1e)(BF_4)]	28.8 (469[s])[d]	25a
[Ag(L1a)(ClO_4)]	11.0 (503[s])[d]	25
[Ag(L1b)(ClO_4)]	58.2 (469[s])[d]	25
[Ag(L1c)(ClO_4)]	9.7 (493[s])[f,g]	25b
[Ag(L1e)(ClO_4)]	28.0 (469[s])[d]	25a
[Ag(L1a)(NO_3)]	7.98 (461,[s] 536[t])[d,g]	23
[Ag(L1a)(NO_3)]	8.07 (460,[s] 533[t])[d,g]	25
[Ag(L1b)(NO_3)]	53.1 (444[s])[d]	25
[Ag(L1c)(NO_3)]	7.2 (475[s])[f,g]	25b
[Ag(L1e)(NO_3)]	23.9 (463[s])[d]	25a
trans-[Ag{$(3\text{-}C_6H_4PPh_2)_2$-α-cyclodextrin}]	14.2 (495)[d]	30
trans-[Ag{$(Ph_2P)_2$-substituted calix[4]-arene}]BF_4	10.4 (503,[s] 580[t])[d]	29
trans-[Ag(L[1])]BF_4	−0.93 (542,[s] 469[t])[d]	28
uncoordinated ligands		
pop	−9.12[i]	62
pop	−9.65[i]	27
dpdo	21.8[f]	72
dph	−15.5[d,w]	102
dphp	−16.0[d,w]	102
dpo	−15.6[d,w]	102
dpn	−15.65[d,w]	102
dpd	−15.7[d,w]	102
dpu	−15.5[d,w]	102
dpdod	−15.65[d,w]	102
dphd	−15.5[d,w]	102
L1a	−8.7[d]	18
L1b	35.6[f]	19
L1d	−8.6[f]	19
L1e	3.8[f]	19
L1f	−9.0[f]	19
L1g	−11.6[f]	19
bdpbz	−15.8[l]	45
bdpps	−13.7[b]	46
bdtps	−29.9[b]	46
bdpbz	−15.8[b]	46
$Ph_2P(m\text{-}C_6H_4)O(CH_2O)_2(m\text{-}C_6H_4)PPh_2$	−15.48[d]	64

Table 1 (Continued)

complex name	δ (^1J(M−^{31}P))[a] ppm (Hz)	ref
$Ph_2P(m\text{-}C_6H_4)O(CH_2O)_3(m\text{-}C_6H_4)PPh_2$	−15.41[d]	64
$PhMeP(m\text{-}C_6H_4)O(CH_2O)_2(m\text{-}C_6H_4)PPhMe$	−34.84, −34.89[d]	64
$Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$	−21.68[d]	90
$1,2\text{-}(Ph_2P(CH_2CH_2O)_2)_2C_6H_4$	−21.71[d]	90
$Ph_2P(CH_2)_6P(Et)(Ph)$	15.48, 17.44[d]	48
$Ph(Et)P(CH_2)_6P(Et)(Ph)$	16.3[d]	48
Y(O)[x]	−19.8[f]	81
Y(S)[x]	−20.3[f]	81
$(Ph_2P)_2$-substituted calix[4]arene}	−6.4[d]	29
$(3\text{-}C_6H_4PPh_2)_2$-α-cyclodextrin	−4.5[d]	30
$(4\text{-}C_6H_4PPh_2)_2$-α-cyclodextrin	−6.8[d]	30

[a] Unless otherwise noted, relative to 85% H_3PO_4. [b] Measured in CD_2Cl_2. [c] Measured at 173 K. [d] Measured in $CDCl_3$. [e] Measured in acetone-d_6. [f] Solvent not reported. [g] Reference not reported. [h] Measured in CD_3CN. [i] Measured in C_6D_6. [j] Referenced vs external triphenyl phosphate (δ − 18). [k] Measured at 34 °C. [l] Measured in CH_2Cl_2. [m] Assigned to PPh_3. [n] Measured in toluene. [o] Measured at 0 °C. [p] Measured at −23 °C. [q] Measured in CH_2Cl_2/acetone-d_6 (4:1). [r] d = doublet, t = triplet. [s] [$^1J(^{107}Ag-^{31}P)$ (Hz)]. [t] [$^1J(^{109}Ag-^{31}P)$ (Hz)]. [u] Measured at 250 K. [v] Measured at 243 K. [w] These values conflict (in sign) with those reported in ref 41. [x] For ligand abbreviation, see Figure 16. [y] Not reported.

Table 2. Dipole Moments for *trans*-Spanning Diphosphine and Related Complexes

complex name	dipole moment μ (Debye)	ref
$[Co\{(C_6H_{11})_2P(CH_2)_5P(C_6H_{11})_{22}\}I_2]$	10.11[a]	4
$[Co\{Ph_2PC_2H_4OC_2H_4PPh_2\}I_2]$	4.61[b]	103
$[Co\{(C_6H_{11})_2PC_4H_8P(C_6H_{11})_2\}I_2]$	3.52[b]	103
$[Co\{Ph_2PC_2H_4OC_2H_4PPh_2\}Br_2]$	4.55[b]	103
$[Co\{Ph_2PC_4H_8PPh_2\}Br_2]$	4.5[b]	103
$[Co\{Ph_2PC_5H_{10}PPh_2\}Br_2]$	4.49[b]	103
$[Co\{(C_6H_{11})_2PC_4H_8P(C_6H_{11})_2\}Br_2]$	4.59[b]	103
$[Co\{(C_6H_{11})_2PC_5P_{10}P(C_6H_{11})_2\}Br_2]$	4.38[b]	103
$[Co\{Ph_2PC_2H_4OC_2H_4PPh_2\}Cl_2]$	4.5[b]	103
$[Co\{(C_6H_{11})_2PC_5P_{10}P(C_6H_{11})_2\}Cl_2]$	4.72[b]	103
$[Co\{Ph_2PC_2H_4OC_2H_4PPh_2\}(NCS)_2]$	4.41[b]	103
$[Ni\{Ph_2PC_2H_4OC_2H_4PPh_2\}I_2]$	3.24[b]	103
$[Ni\{Ph_2PC_2H_4OC_2H_4PPh_2\}Br_2]$	3.23[b]	103
$[Ni\{(C_6H_{11})_2P(CH_2)_5P(C_6H_{11})_2\}Cl_2]$	2.37[a]	4
$[Ni\{(C_6H_{11})_2PC_5P_{10}P(C_6H_{11})_2\}Cl_2]$	0.0[b]	103
$[Ni\{Ph_2PC_2H_4OC_2H_4PPh_2\}Cl_2]$	3.26[b]	103
$[Ni\{Ph_2PC_2H_4OC_2H_4PPh_2\}(NCS)_2]$	0.0[b]	103

[a] In benzene. [b] Reference not reported.

NMR spectroscopy.[25] The X-ray crystal structures of [Ag(L1b)Cl], [Ag(L1b)Br], and [Ag(L1b)ClO_4] have P(1)−Ag−P(2) angles of 142.6(1)°, 141.6(2)°, and 161.6(1)°, respectively, indicating serious distortions from idealized trigonal planar or T-shaped geometries.[25] While the crystal structures of [Ag(L1b)Cl] and [Ag(L1b)Br] indicate the covalent character of the Ag−X bond, the structure of [Ag(L1b)ClO_4] indicates ionic character in the Ag−O (O from ClO_4^-) bond. Notably, the P(1)−Ag−P(2) angle of [Ag(L1b)-ClO_4] is 10° larger than that of [Ag(L1a)ClO_4] and the Ag−O (O from ClO_4^-) bond length is 0.13 Å greater in the L1b complex than in the L1a complex. While these increases could derive from the presence of the sterically bulkier *t*-Bu groups in the L1b ligand, the difference in the P(1)−Ag−P(2) angle decreases by ca. 2° for the chloride analogues (142.6° and 140.7° for the L1b and L1a complexes, respectively). Thus, the crystallographic data does not provide compelling evidence to indicate that changes in the geometry about the silver metal center are due to the sterically more demanding nature of L1b over L1a.[25] Changes in the identity of the anion also strongly affect the silver−phosphorus coupling constants, $^1J(^{107}Ag^{31}P)$, but the coupling constant data are not readily correlated among the L1a-, L1b-, and L1c-containing silver chloride and perchlorate complexes.[25]

Finally, complexes of the type [Pt(L1a)Y], where Y = C_2H_4, $CH_2{=}CHCO_2Me$, $PhC{\equiv}CPh$, $MeC{\equiv}CMe$, $MeO_2CC{\equiv}CCO_2Me$, $(i\text{-}Pr)O_2CC{\equiv}CCO_2(i\text{-}Pr)$, PPh_3, and CO, were prepared for comparison to the corresponding species, [Pt(L1a)$(PPh_3)_2$].[26] The reaction of L1a with [Pt$(C_2H_4)_3$] generated in situ from [Pt-$(COD)_2$] resulted in the formation of [Pt(L1a)$(C_2H_4)]_x$, where x = 1 or 2. Mononuclear and binuclear product formation could be distinguished due to low solubility, dissociation, and air sensitivity. The complexes [Pt(L1a)$(CH_2{=}CHCO_2Me)$], [Pt(L1a)(PPh_3)], [Pt(L1a)-(CO)], and the other olefin and alkyne analogues were readily prepared from [Pt(L1a)$(C_2H_4)]_x$, *trans*-[Pt(CH_3CN)(L1a)H][BF_4], and/or [Pt$(COD)_2$].[26] The [Pt(L1a)$(CH_2{=}CHCO_2Me)$] complex demonstrated a broad, room temperature ^{31}P NMR spectrum that indicated either an incipient fluctional or dissociative process**.** Finally, the platinum complex, [Pt(L1a)(O_2)-(acetone)], was obtained in high yield from an oxygenated acetone solution of [Pt(L1a)$(PPh_3)]_x$.[26] These syntheses demonstrate the ability to form multiple platinum(L1a) starting materials for potential catalytic activities.

Table 3. Crystal Structure Data for *trans*-Spanning Diphosphine and Related Complexes

complex name	P(1)−M−P(2) angle (deg)	M−P lengths (Å)	ref
$[Cu(PPh_3)_2Br]$	126.0(1)	2.282(3), 2.263(3)	22
[Cu(L1a)Cl]	131.9(1)	2.258(2), 2.217(4)	22
$[Au(PPh_3)_2Br]$	132.1(1)	2.323(4), 2.339(4)	22
trans-[Au(L1a)Cl]	175.7(1)	2.307(2), 2.310(2)	22
trans-[Ir(L1a)(CO)Cl]	173.9(2)	2.310(4), 2.310(4)	55
trans-[Ir(L1a)(CO)Cl_3]	170.7(1)	2.403(3), 2.419(3)	55
trans-[Ir{*t*-$Bu_2PC{\equiv}C(CH_2)_5C{\equiv}CPt$-$Bu_2$}(CO)Cl]	164.15(6)	2.332(2), 2.337(2)	79
[Ir(CO)Cl{ClPb(crown-P_2)}]Cl·$2CH_2Cl_2$	165.0(3)	2.331(8), 2.334(8)	51
[Ir(CO)Cl{ClSn(crown-P_2)}][$SnCl_3$]	161.8(2)	2.291(7), 2.363(6)	51
[Ir(CO)I{K(crown-P_2)}]I·$3CH_2Cl_2$	168.4(2)	2.319(7), 2.316(7)	51
trans-[Mo{$Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$}$(CO)_4$]	175.69(4)	2.472(1), 2.484(1)	88
[Ni(poop)I_2]	161(0.4)	2.242(11), 2.244(10)	70
trans-[Ni(dpdo)$(NCS)_2$]	175.9(1)	2.240(3), 2.233(3)	68
trans-[Pd(L1a)Cl_2]	175.7(1)	2.326(2), 2.322(2)	54
trans-[Pd(dpdo)I_2]	164.9(1)	2.330(2), 2.321(2)	72
cis-[Pt(L1a)Cl_2]	104.8(1)	2.253(3), 2.256 (2)	56
trans-[Pt{$Ph_2P(o$-$C_6H_4)NHC(O)$(2,6-pyridine)$C(O)NH(o$-$C_6H_4)PPh_2$}Cl_2]	174.43(5)	2.3212(12), 2.3196(12)	80
trans-[Pt(L1a)ClH]	176.2(1)	2.282(3), 2.278(3)	59
[Rh(L1a)(CO)Cl]	174.7(1)	2.317(3), 2.313(3)	54
[Rh{*t*-$Bu_2P(CH_2)_4C{\equiv}C(CH_2)_4Pt$-$Bu_2$}(CO)Cl]	171.6(2)	2.345(7), 2.352(7)	77
[Rh{*t*-$Bu_2P(CH_2)_2C{=}C(CH_2)_2Pt$-$Bu_2$}(CO)Cl]	176.0(2)	2.323(5), 2.309(5)	77
[Rh{$Ph_2P(CH_2)_2O(CH_2)_2PPh_2$}(CO)]	165.9(1)	2.307(2), 2.294(2)	64
[Rh(H_2O){$Ph_2P(CH_2)_2O((CH_2)_2O)_2(CH_2)_2PPh_2$}(CO)]	174.3(1)	2.334(3), 2.343(2)	64
[Rh{$Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$}(CO)][$PF_6$]	178.6(2)	2.340(4), 2.331(4)	66
[Ru(L1a)(CO)Cl(NO)]	167.4(1)	2.410(2), 2.391 (2)	86
cis,*cis*,*trans*-[Ru{$Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$}$(CO)_2Cl_2$]	177.70(8)	2.420(2), 2.406(2)	91
cis,*cis*,*trans*-[Ru{μ-$Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$}$(CO)_2Cl_2$]·$Me_2CO$	171.65(8)	2.413(2), 2.404(3)	91
trans-[RuCl(trpy)$(PPh_3)_2$][BF_4]·CH_2Cl_2	178.1(1)	2.398(2), 2.415(2)	87
trans-[Ru(C4SPAN)Cl(trpy)][PF_6]·$0.25C_6H_5Me$, $0.5CH_2Cl_2$	175.0(1)	2.397(2), 2.397(2)	97
trans-[Ru(L1a)Cl$(NO)_2$](BF_4)	164.1(1)	2.455(2), 2.439(2)	87
trans,*trans*,*trans*-[Ru$(CO)_2Cl_2${$(Ph_2P)_2$-substituted calix[4]arene}]	172.2(3)	2.209(5), 2.403(5)	29
[Ag(L1b)Br]	141.6(2)	2.463(4), 2.433(5)	25
[Ag(L1a)Cl]	140.7(1)	2.458(3), 2.411(3)	22
[Ag(L1b)Cl]	142.6(1)	2.457(2), 2.427(2)	25
[Ag(pop)Cl]·$0.5(CH_3)_2CO$·$0.5C_6H_{12}$	145.61(8)	2.435(3), 2.400(3)	27
[Ag(L1a)($SnCl_3$)]	142.2(1)	2.419(3), 2.451(3)	24
[Ag(L1a)(NO_3)]	148.6(1)	2.424(2), 2.410(2)	24
[Ag(L1a)(ClO_4)]	151.5(1)	2.417(3), 2.401(3)	24
[Ag(L1b)(ClO_4)]	161.5(1)	2.394(2), 2.393(2)	25
[Ag(L1c)(ClO_4)]—Molecule 1	167.6(1)	2.389(3), 2.393(3)	25b
[Ag(L1c)(ClO_4)]—Molecule 2	164.8(1)	2.377(3), 2.378(3)	25b

To determine the effect of the rigidity of the preformed span, Kapoor and co-workers synthesized the Ag(pop)Cl complex for comparison with Ag(L1a)Cl.[27] The molecular structure of Ag(pop)Cl closely resembles that of Ag(L1a)Cl. The Ag atom is three-coordinate with the AgP_2Cl central coordination unit in a planar configuration. The arrangement of the donor atoms is intermediate between a trigonal planar and T-shaped geometry with P(1)−Ag−P(2) = 145.61(8)° for the more flexible pop ligand and 140.7(1)° for the more rigid L1a ligand.[27] Thus, the less rigid pop ligand prefers larger P(1)−Ag−P(2) bond angles than the flexible L1a ligand.

Further efforts with preformed *trans*-spanning ligands focused on strapping a transition-metal center across the mouth of a calix[4]arene backbone. This approach requires a suitable coordinating moiety on the distal sites, and toward this end, terminal phosphine moieties were used by Matt and co-workers.[28,29] These ligands have short pendent arms in order to maximize localization of the metal center and are attached at the phenolic oxygen atoms, leaving two further sites where secondary coordination moieties may be appended. The compound 5,11,17,23-tetra-*tert*-butyl-25,27-di-RCH_2O-26,28-diphenylphosphinomethoxy)calix[4]arene (R = $C(O)NEt_2$ = L^1) has been reacted with [Au(THF)(SC_4H_8)]BF_4 (where THF = tetrahydrofuran and SC_4H_8 = tetrahydrothiophene) and $AgBF_4$ to yield the chelate complexes, *trans*-[AuL^1]BF_4 and [AgL^1]BF_4, respectively (Figure 5).[28,29] The FAB-mass spectrum of *trans*-[AuL^1]BF_4 indicates the complex is mononuclear, and the NMR spectra are consistent with a C_2-symmetrical structure with a linear AuP_2^+ arrangement. The *trans*-[AgL^1]BF_4 complex also demonstrated an NMR spectrum consistent with equivalence of both of the phosphine arms as well as both amide groups. Notably, the solution-phase IR spectrum of *trans*-[AuL^1]BF_4 in THF showed one absorption band in the carbonyl region, whereas for the *trans*-[AgL^1]BF_4 complex, two bands were observed. The authors interpret this difference to mean that the *trans*-[AuL^1]BF_4 complex has amide groups that are uncomplexed to the metal center while the two amide groups in *trans*-[AgL^1]BF_4 are in different environments as induced by the silver cation.[28] They propose that one of the carbonyl groups is weakly bound to the silver and suggest that the two amides alternate coordination on a time scale that is faster than that which can be measured by NMR spectroscopy.[28] The tight binding constraint imposed by the diphosphine requires that additional complexation with the car-

Table 4. IR Spectroscopy[a] for *trans*-Spanning Diphosphine and Related Complexes

complex name	ν(M−X) (cm^{-1})	ν(CO) (cm^{-1})	ν(NO) (cm^{-1})	ν(M−H) (cm^{-1})	ref
$[Fe(CO)_3(PPh_3)_2]$		1882[b]			83
[Fe(L1a)(CO)$_3$]		1869, 1898, 1976			83
$[Fe(Ph_2PCH_2Ph)_2(CO)_3]$		1858, 1888, 1967			83
trans-[Ir(L1a)(CO)I]		1970[b]			53
trans-[Ir(L1a)(CO)(NCS)]		1980[b]		2090[c]	53
trans-[Ir(L1a)Br(CO)Br]		1965[b]			53
trans-[Ir(dpd)Br(CO)]	252[d]	1965			42
trans-$[Ir(Ph_2PCH_2Ph)_2(CO)Cl]$		1965[b]			53
trans-[Ir(L1a)(CO)Cl]		1965[d]			53/101
trans-[Ir(CO)Cl(dpd)]	302d[b]	1975			42
[Ir(bdpbz)(CO)Cl]	310	1958			45
trans-$[Ir((CH_3CN)(L1a)(CO)][BF_4]$		2000[b]			53
$[Ir(L1a)(CO)HI_2]$		2030[b]		2160	53
$[Ir(L1a)Br_2(CO)H]$		2035[b]		2180	53
$[Ir(Ph_2PCH_2Ph)_2(CO)Cl_2H]$		2050[b]		2120	53
$[Ir(L1a)(CO)Cl_2H]$		2025[b]		2175	53
$[Ir(L1a)(CO)H_2I]$		2000[b]		2120, 2175[e]	53
$[Ir(CH_3CN)(L1a)(CO)H_2][BF_4]$		2010		2120, 2200	53
$[Ir(L1a)(CO)_2H_2][BF_4]$		2045[b]		2080, 2155	53
$[Ir(Ph_2PCH_2Ph)_2(CO)_2H_2][BF_4]$		2040[b]		2075, 2145	53
$[Ir(CO)Cl\{(crown\text{-}P_2)\}]$		1957			51
$Ir(CO)Cl[\{CH_3CO_2Pb(crown\text{-}P_2)\}](CH_3CO_2)$		1974			51
$[Ir(CO)Cl\{ClPb(crown\text{-}P_2)\}]Cl$		1977			51
$[Ir(CO)Cl\{ClPb(crown\text{-}P_2)\}][BPh_4]$		1979, 1969			51
$[Ir(CO)Cl\{ClSn(crown\text{-}P_2)\}](SnCl_3)$		1974			51
$[Ir(CO)Cl\{Na(crown\text{-}P_2)\}][BPh_4]$		1964			51
$[IrBr(CO)Br\{Na(crown\text{-}P_2)\}]Br$		1963			51
$[Ir(CO)\{Na(crown\text{-}P_2)\}I]I$		1961			51
$[Ir(CO)Cl\{K(crown\text{-}P_2)\}][PF_6]$		1970			51
$[Ir(CO)I\{K(crown\text{-}P_2)\}]I$		1969			51
$[Ir(CO)Cl\{Pb(crown\text{-}P_2)\}][BPh_4]$		2013			51
trans-$[Ni(dpo)I_2]$	230[d]				42
trans-$[Ni(dpd)I_2]$	220[d]				42
trans-$[NiBr_2(dpo)]$	262[d]				42
trans-$[NiBr_2(dpd)]$	258[d]				42
$[NiBr_2(dpdo)]$	340[f]				68
trans-$[NiBr_2(pop)]$	326[g]				27
trans-$[NiCl_2(dpo)]$	339[d]				42
trans-$[NiCl_2(dpd)]$	337[d]				42
trans-$[Ni(pop)Cl_2]$	408[g]				26
trans-$[Ni(NCS)_2(pop)]$				2080[c,g]	27
trans-[Ni(L1a)(NCS)$_2$]				2086[c,g]	27
trans-$[Ni(pop)(CN)_2]$				2110[c,g]	27
trans-$[Pd\{t\text{-}Bu_2P(CH_2)_{12}Pt\text{-}Bu_2\}Cl_2]_2$	346				37
trans-$[Pd\{t\text{-}Bu_2P(CH_2)_{12}Pt\text{-}Bu_2\}Cl_2]$	345				37
trans-$[Pd\{t\text{-}Bu_2P(CH_2)_{10}Pt\text{-}Bu_2\}Cl_2]_2$	347				37
trans-$[Pd\{t\text{-}Bu_2P(CH_2)_{10}Pt\text{-}Bu_2\}Cl_2]$	341				26
trans-$[Pd(pop)Cl_2]$	360[g]				27
trans-$[Pd\{Ph_2P(CH_2)_{12}PPh_2\}Cl_2]$	342[h]				43
trans-$[Pd\{Ph_2P(CH_2)_{12}PPh_2\}(NCS)_2]\cdot 0.5CHCl_3$				2076[c,h]	43
trans-$[PdCl_2\{Y(O)\}]$[k]	348[d]				81
trans-$[CaPdCl_2\{Y(O)\}]$[k]	314, 281[d]				81
cis-$[CuPdCl_2\{Y(O)\}]$[k]	313, 278[d]				81
trans-$[Pt\{t\text{-}Bu_2P(CH_2)_{12}Pt\text{-}Bu_2\}Cl_2]_3$	333				37
trans-$[Pt\{t\text{-}Bu_2P(CH_2)_{12}Pt\text{-}Bu_2\}Cl_2]_2$	334				37
trans-$[Pt\{t\text{-}Bu_2P(CH_2)_{12}Pt\text{-}Bu_2\}Cl_2]$	332				37
trans-$[Pt\{t\text{-}Bu_2P(CH_2)_{10}Pt\text{-}Bu_2\}Cl_2]_2$	334				31/37
trans-$[Pt\{t\text{-}Bu_2P(CH_2)_{10}Pt\text{-}Bu_2\}Cl_2]$	326				31/37
trans-$[Pt\{t\text{-}Bu_2P(CH_2)_9Pt\text{-}Bu_2\}Cl_2]_2$	333				37
trans-$[Pt\{t\text{-}Bu_2P(CH_2)_9Pt\text{-}Bu_2\}Cl_2]$	328				37
trans-$[Pt(L1d)(CO_2H)H]$				2255	59
trans-[Pt(L1a)ClH]				2262	59
trans-[Pt(L1d)ClH]				1790	58
trans-[Pt(L1d)ClH]				2250−2290	58
trans-$[Pt\{P(CH_2Ph)(p\text{-}PhCF_3)_2\}_2ClH]$				2200	58
trans-[Pt(L1d)H(4-PADA)][BF$_4$]			2220		58
trans-$[Pt(L1d)(CO)Me][BF_4]$		2130			59
trans-$[PtCl_2(dpe)]$	340				41
trans-$[PtCl_2(dph)]$	340				41
trans-$[PtCl_2(dphp)]$	340				41
trans-$[PtCl_2(dpo)]$	338				41

Table 4 (Continued)

complex name	ν(M−X) (cm^{-1})	ν(CO) (cm^{-1})	ν(NO) (cm^{-1})	ν(M−H) (cm^{-1})	ref
trans-[$PtCl_2$(dpn)]	340				41
trans-[$PtCl_2$(dpd)]	340				41
trans-[$PtCl_2$(dpdo)]	338				72
trans-[Pt(dpdo)(NCS)(SCN)]	280[i]				72
trans-[Pt(L1d)ClH]				2250−2290	58
trans-[Pt(L1d)H(4-PADA)]				2220	58
cis-[$PtCl_2${Y(O)}][k]	318, 281[d]				81
trans-[$PtCl_2${Y(O)}][k]	314, 281[d]				81
trans-[Rh(L1a)(CO)I]		1980[b]			53
trans-[Rh(L1a)Br(CO)]		1980[b]			53
trans-[RhBr(CO)(dpd)]	220[d]	1955			42
trans-[Rh($Ph_2PCH_2Ph)_2$(CO)Cl]		1970[b]			53
trans-[Rh($Ph_2PCH_2Ph)_2$(CO)Cl][BF_4]		2000[b]			53
trans-[Rh(L1a)(CO)Cl]		1980[b]			53
trans-[RhCl(CO)(dpd)]	310[d]	1975			42
trans-[RhCl(CO)(dphd)]	305[d]	1970			42
[RhCl(CO)(bdpbz)]	311	1970			45
trans-[Rh(L1a)(CO)(NCS)]		1990[f]		2090[j]	53
trans-[Rh(CH_3CN)(L1a)(CO)][BF_4]		2010[f]			53
trans-[Rh(CO)Cl{(3-$C_6H_4PPh_2)_2$-α-cyclodextrin}]		1977[j]			30
[Ru$(CO)_3(PPh_3)_2$]		1900			83
[Ru(L1a)$(CO)_3$]		1880, 1910, 1980[j]			83
[Ru($Ph_2PCH_2Ph)_2(CO)_3$]		1872, 1900, 1970[j]			83
[RuCl(NO)$(PPh_3)_2$]			1762[d]		86
[Ru($Ph_2PhCH_2Ph)_2$Cl(NO)]			1740[j]		86
[Ru(L1a)Cl(NO)]			1720		86
trans-[Ru(L1a)Cl(NO)]			1722[d]		87
[Ru(CO)Cl(NO)$(PPh_3)_2$]		1925	1720[d]		86
[Ru($Ph_2PhCH_2Ph)_2$(CO)Cl(NO)]		1920	1605[j]		86
[Ru(L1a)(CO)Cl(NO)(L1a)]		1915	1672		86
trans-[Ru(L1a)Cl$(NO)_2$][BF_4]			1810, 1760[d]		87
[Ru(L1a)Cl(NO)($P(OCH_2)_3$−CC_2H_5)]			1654		86
cis,cis,trans-[Ru{$Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$}-$(CO)_2Cl_2$]	2058, 1995[j]				91
cis,cis,trans-[Ru{μ-$Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$}-$(CO)_2Cl_2$]	2058, 1995[j]				91
cis,cis,trans-[Ru{$Ph_2P(CH_2CH_2O)_5CH_2CH_2PPh_2$}-$(CO)_2Cl_2$]	2058, 1997[j]				91
cis,cis,trans-[Ru{1,2-($Ph_2P(CH_2CH_2O)_2)_2C_6H_4$}-$(CO)_2Cl_2$]	2058, 1994[j]				90
cis,cis,trans-[$Ru(CO)_2Cl_2${($Ph_2P)_2$-substituted calix[4]arene}]	2072, 1995				29
trans,trans,trans-[$Ru(CO)_2Cl_2${($Ph_2P)_2$-substituted calix[4]arene}]	1924				29

[a] Unless otherwise noted, Nujol mull was used. [b] Solution spectrum in $CHCl_3$. [c] ν(CN). [d] Method not specified. [e] Shoulders at 2190 and 2100 cm^{-1} were also observed. [f] Solution spectrum in CH_2Cl_2. [g] CsBr pellets or Nujol suspensions. [h] Nujol and hcb. [i] ν(M−S). [j] KBr disk. [k] Ligands Y(O) and Y(S) are defined in Figure 16.

bonyl group forms a Y-shaped (rather than T-shaped) geometry.

Using the bis(diphenylphosphino)α-cyclodextrins, Matt and co-workers also investigated the coordination of silver(I) and gold(I) cations to form *trans-P,P′*-chelates.[30] The reported characterization of these linear complexes was limited to NMR spectroscopy and FAB-mass spectrometry.

B. Preformed Square Planar or Distorted Square Planar Complexes

1. Alkyl Linkages

As mentioned earlier, Isslieb and Hohlfeld prepared the first *trans*-spanning complexes during their investigation of the use of $(C_6H_{11})_2P(CH_2)_nP(C_6H_{11})_2$ ligands.[4] They produced complexes of the type [M($(C_6H_{11})_2P(CH_2)_nP(C_6H_{11})_2$)$X_2$] (where M = Ni, Co, and Fe; n = 3, 4, and 5; X = Cl^-, Br^-, I^-, and NO_3^-) as well as [Cu($(C_6H_{11})_2P(CH_2)_3P(C_6H_{11})_2$)Br] and [$Cu_2$-($(C_6H_{11})_2P(CH_2)_5P(C_6H_{11})_2$)$Br_2$]. While the cobalt complexes had a tetrahedral configuration and the copper complexes existed as either three-coordinate or dimeric species, the nickel complexes were monomolecular and diamagnetic, indicative of planar structures. With n = 3 (X = Br^-), the dipole moment of the nickel complex was 11.13 D, but with n = 5 (X = Cl^-), the dipole moment was only 2.37 D. Isslieb and Hohlfeld interpreted this difference in the dipole moments to indicate that in the latter compound, the methylene chain reaches across the coordination plane, producing the first square planar, *trans*-spanning diphosphine. Some authors questioned the assignment of the square planar geometries to these nickel complexes due to the relatively short chain length of the spanning linkage.[8,31]

The formation of large size *trans*-spanning rings (12 or 13 atoms) has been a subject of some debate. Some authors suggested that mononuclear bidentate complexes with large rings (12 or 13 atoms) might

Table 5. Electronic Spectroscopy for *trans*-Spanning Diphosphine and Related Complexes

complex name	UV−Vis spectroscopy λ_{max} (nm, $10^{-4}\epsilon$ (M^{-1} cm^{-1}))	ref
[Ir(CO)Cl{crown-P_2}]	434, 384, 334[a,b]	51
[Ir(CO)Cl{Na(crown-P_2)}][BPh_4]	431 (0.044), 380 (0.23), 335 (0.21)[a]	51
[Ir(CO)Br{Na(crown-P_2)}]Br	436 (0.048), 383 (0.22), 341 (0.19)[a]	51
[Ir(CO)I{Na(crown-P_2)}]I	442 (0.061), 390 (0.21), 346 (0.20)[a]	51
[Ir(CO)Cl{K(crown-P_2)}][PF_6]	426 (0.050), 376 (0.284), 336 (0.234)[a]	51
[Ir(CO)I{K(crown-P_2)}]I	431 (0.069), 386 (0.223), 345 (0.230)[a]	51
[Ir(CO)Cl{Pb(crown-P_2)}][BPh_4]	476 (0.077), 376 (1.73)[a]	51
[Ir(CO)Cl{CH_3CO_2Pb(crown-P_2)}](CH_3CO_2)	456 (0.056), 394 (1.52)[a]	51
[Ir(CO)Cl{ClPb(crown-P_2)}]Cl	470 (0.065), 394 (1.97), 310 (0.605)[a]	51
[Ir(CO)Cl{ClPb(crown-P_2)}][BPh_4]	470 (0.026), 396 (2.17), 310 (0.50)[a]	51
[Ir(CO)Cl{ClPb(crown-P_2)}][$SnCl_3$]	504 (0.031), 422 (2.38)[a]	51
[Ni{$Ph_2P(CH_2)_5PPh_2$}I_2]	2000, 1190 (sh), 926, 578 (sh)[c]	76
trans-[Ni(pop)I_2]	617 (0.0509), 400 (sh), 345 (0.766), 298 (1.96), 260 (sh)[a]	27
trans-[Ni(dpo)I_2]	633 (0.0026), 500 (0.0198)[d]	42
trans-[Ni(dpd)I_2]	595 (0.0030), 457 (0.0240)[d]	42
trans-[Ni(poop)I_2]	972 (0.0575), 663 (0.2454), 573 (0.4786)[e]	69
[Ni(POP)I_2]	2000, 917 (0.0565), 649 (sh), 442 (0.456)[f]	76
[Ni(dpdo)I_2]	228 (1.217), 340 (sh), 388 (sh), 455 (0.206), 671 (0.0363)[a]	68
[Ni{$(C_5H_{11})_2P(CH_2)_3P(C_5H_{11})_2$}$Br_2$]	328 (3.3), 656 (4.4), 1312 (5.9)[g]	4
[Ni{$Ph_2P(CH_2)_5PPh_2$}Br_2]	2000, 1124 (sh), 893, 571, 417[c]	76
trans-[Ni(pop)Br_2]	549 (0.0428), 405 (0.863), 326 (sh), 296 (sh), 267 (sh), 251 (3.01)[a]	27
trans-[$NiBr_2$(dpo)]	581 (0.0067), 420 (0.0288)[d]	42
trans-[$NiBr_2$(dpd)]	552 (0.0064), 441 (0.0838)[d]	42
[Ni(POP)Br_2]	2000, 1136 (sh), 870 (0.0245), 559 (0.0158), 460 (0.5650)[f]	76
[$NiBr_2$(dpdo)]	272 (0.957), 402 (0.236), 602 (0.0254)[f]	68
[Ni{$(C_5H_{11})_2P(CH_2)_5P(C_5H_{11})_2$}$Cl_2$]	234 (9.9)[g]	4
trans-[Ni(pop)Cl_2]	494 (0.0421), 379 (1.540), 290 (sh), 275 (sh), 266 (1.330), 245 (sh)[a]	27
trans-[$NiCl_2$(dpo)]	549 (0.0090), 400 (0.0930)[d]	42
trans-[$NiCl_2$(dpd)]	552 (0.0087), 407 (0.1090)[d]	42
[Ni(POP)Cl_2]	1667 (0.0028), 1235 (sh), 1053, 855 (0.0133), 535 (0.0127), 389 (0.566)[f]	76
trans-[Ni(pop)$(NCS)_2$]	500 (sh), 394 (0.976), 312 (2.20), 285 (1.19), 275 (1.19), 247 (sh)[a]	27
trans-[Ni(dpo)$(NCS)_2$]	392 (0.0126), 309 (0.1740)[d]	42
[Ni(dpo)$(NCS)_2$]	382, 441(sh)[c]	71
trans-[Ni(dpd)$(NCS)_2$]	392 (0.0126), 313 (0.1780)[d]	42
[Ni(dpdo)$(NCS)_2$]	300 (1.267), 382 (0.937)[a]	68
trans-[Ni(pop)$(CN)_2$]	350 (sh), 312 (sh), 295 (1.60), 275 (3.04), 260 (sh)[a]	27
trans-[Pd{$Ph_2P(CH_2)_{12}PPh_2$}I_2]	323 (1.520), 420 (0.441)[d]	43
trans-[Pd{$Ph_2P(CH_2)_{12}PPh_2$}Br_2]	295 (0.923), 362 (1.107)[d]	43
trans-[Pd{$Ph_2P(CH_2)_{12}PPh_2$}Cl_2]	340 (1.318)[d]	43
trans-[Pd{$Ph_2P(CH_2)_{12}PPh_2$}$(NCS)_2$]·0.5 $CHCl_3$	303 (1.376), 340 (1.290)[d]	43
trans-[Pd(pop)I_2]	421 (0.332), 327 (1.39), 292 (sh), 270 (2.01)[a]	27
trans-[Pd(pop)Cl_2]	335 (1.88), 287 (sh), 274 (0.925), 266 (sh)[a]	27
trans-[Pd(pop)Br_2]	358 (1.21), 306 (1.05), 292 (sh), 275 (sh)[a]	27
trans-[Pd(dpdo)I_2]	327 (0.9515)[d]	72
trans-[Pd(dpdo)$(NCS)_2$]	474 (0.1940)[d]	72
trans-[Pt(poop)I_2]	348 (0.251), 301 (0.708), 272 (sh)[a]	69
trans-[Pt(dpdo)I_2]·KCl	331 (sh)[d]	72
trans-[Pt(pop)Br_2]	342 (sh), 290 (1.11), 275 (sh)[a]	27
trans-[Pt(pop)Cl_2]	315 (sh), 275 (1.98)[a]	27
trans-[$PtCl_2$(dpdo)]	271 (0.846)[d]	72
trans-[Pt{$P(CH_2Ph)(p\text{-}PhCF_3)_2$}$_2$H(4-PADA)][$BF_4$]	505 (4.4)[a]	58
trans-[Pt(L1d)H(4-PADA)][BF_4]	510 (4.0)[a]	58
trans-[Pt{$P(CH_2Ph)(p\text{-}PhCF_3)_2$}$_2$Me(4-PADA)][$BF_4$]	507 (4.2)[a]	58
trans-[Pt(L1d)Me(4-PADA)][BF_4]	510 (4.3)[a]	58
trans-[Rh(pop)(CO)Cl]	363 (0.339), 274 (1.40)[a]	27
trans-[RuCl(trpy)(PPh_3)$_2$][PF_6]	473 (0.362), 431 (sh), 330 (sh), 312 (2.32), 268 (4.32)[h]	96/97
trans-[Ru(C3SPAN)Cl(trpy)][PF_6]	473 (0.35), 432 (sh), 334 (sh), 311 (2.17), 271 (3.85), 232 (5.21)[h]	97
trans-[Ru(C4SPAN)Cl(trpy)][PF_6]	473 (0.384), 432 (sh), 334 (sh), 311 (2.14), 271 (3.99), 231 (5.10)[h]	97
trans-[Ru(ISPAN)Cl(trpy)][PF_6]	471 (0.41), 432 (sh), 333 (sh), 311 (2.50), 271 (4.20), 233 (7.56)[h]	97
trans-[Ru{$Ph_2PPhCH_2N(CH_3)(CH_2)_6N(CH_3)$-$CH_2PhPPh_2$}Cl(trpy)][$ClO_4$]	470 (0.33)[h]	96
trans-[Ru{$Ph_2PPhCH_2N(CH_3)_2(CH_2)_6N(CH_3)_2$-$CH_2PhPPh_2$}Cl(trpy)][$PF_6$]$_3$	470 (0.33)[h]	96
trans-[Ru{$Ph_2PPhCH_2N(CH_3)(CH_2)_5N(CH_3)$-$CH_2PhPPh_2$}Cl(trpy)][$ClO_4$]	470 (0.35)[h]	96
trans-[Ru{$Ph_2PPhCH_2N(CH_3)_2(CH_2)_5N(CH_3)_2$-$CH_2PhPPh_2$}Cl(trpy)][$PF_6$]$_3$	470 (0.34)[h]	96
trans-[Ru{$Ph_2PPhCH_2N(CH_3)$(*m*-xylene)$N(CH_3)$-CH_2PhPPh_2}Cl(trpy)][ClO_4]	472 (0.66)[h]	96
trans-[Ru{$Ph_2PPhCH_2N(CH_3)_2$(*m*-xylene)$N(CH_3)_2$-CH_2PhPPh_2}Cl(trpy)][ClO_4]$_3$}$_2$	470 (0.65)[h]	96

[a] Measured in CH_2Cl_2. [b] Instability in solution precluded accurate evaluation of ϵ values. [c] Measured in the solid state. [d] Measured in $CHCl_3$. [e] Measured in benzene. [f] Measured in $(CH_2Cl)_2$. [g] Measured in benzonitrile. [h] Measured in CH_3CN.

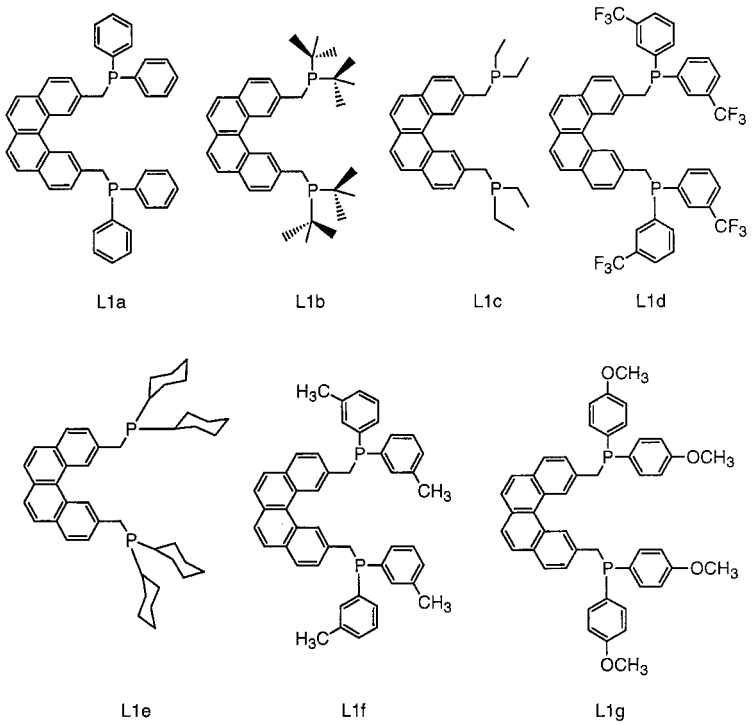


Figure 4. Substituted methylphenylbenzo[*c*]phenanthrene ligands; abbreviations as used in text.

be more stable than those with an intermediate-sized ring (nine-membered rings) due to the increased flexibility of the larger ring size.[31] Other authors asserted that metal complexes containing large chelate rings from flexible ligands would not form.[31,32] Pryde, Shaw, and Weeks demonstrated that the treatment of $[PtCl_2(PhCN)_2]$ with $(t\text{-Bu})_2P(CH_2)_{10}P(t\text{-Bu})_2$ gives two products.[31] The first reaction product was binuclear and gave a well-defined 1:2:1 *t*-Bu ^1H NMR pattern, indicating *trans*-phosphorus nuclei. This binuclear complex also showed a strong infrared absorption band at 334 cm^{-1}, which is characteristic of a linear Cl−Pt−Cl system. It was postulated that the binuclear complex contained a 26-membered ring.[31,33] The second and more soluble complex also gave a 1:2:1 ^1H NMR triplet and a strong infrared band at 326 cm^{-1} in addition to a monomolecular structure in chloroform and an intense parent peak (*m*/*z* 696) in the mass spectrum.[31,33] The authors proposed that this platinum(II) complex contained a *trans*-spanning structure and was likely to have a 13-atom ring.

Generally, long carbon chains are condensed into large rings using dilution techniques or template effects. There are few instances in which larger rings are formed preferentially. Shaw and co-workers showed the use of long-chain diphosphine ligands, $(t\text{-Bu})_2P(CH_2)_nP(t\text{-Bu})_2$ ($n = 9$, 10, or 12), to produce 12−45-membered metal chelate rings (in preference to open-chain polymeric species) (see Figure 6).[34] ^{31}P and ^1H NMR spectroscopies show that there is restricted rotation about P−metal bonds in metal complexes containing the $(t\text{-Bu})_2P(CH_2)_nP(t\text{-Bu})_2$ ligand. Space filling molecular models also show that coordinating one end of the $(t\text{-Bu})_2P(CH_2)_nP(t\text{-Bu})_2$ ligand to a metal halide severely restricts rotations about defined bonds and favors cyclization. The Thorpe−Ingold or "gem-dimethyl" effect may be the cause of these remarkable chelate ring stabilizations. While methyl groups may stabilize small rings and increase the rate at which small carbon rings are formed,[35] Shaw and co-workers proposed that the more bulky *tert*-butyl groups were necessary for phosphorus to have a "gem-*tert*-butyl" ring stabilizing effect. Analogous diphosphine ligands with less bulky groups (e.g., Ph) were initially observed to give open-chain, polymeric structures instead of *trans*-spanning complexes.[34,36] Additionally, Shaw and co-workers proposed that the bulky *tert*-butyl groups hinder the phosphorus donor atoms from taking up mutual *cis*-positions, but they would not hinder them from taking up *trans*-positions.[31]

Three isomers of the type *trans*-$[Pt\{t\text{-Bu}_2P(CH_2)_{12}Pt\text{-Bu}_2\}Cl_2]_x$, where $x = 1-3$, were also prepared, forming 15-, 30-, and 45-atom rings.[33] The X-ray crystal structure of *trans*-$[Pt\{t\text{-Bu}_2P(CH_2)_{12}Pt\text{-Bu}_2\}Cl_2]$ shows one chloride ligand is gauche with respect to the *tert*-butyl groups; while the *trans*-$[Pt\{t\text{-Bu}_2P(CH_2)_9Pt\text{-Bu}_2\}Cl_2]$ complex demonstrated restricted rotation about the P−Pt bond in the NMR spectrum, the *trans*-$[Pt\{t\text{-Bu}_2P(CH_2)_{10}Pt\text{-Bu}_2\}Cl_2]$ and *trans*-$[Pt\{t\text{-Bu}_2P(CH_2)_{12}Pt\text{-Bu}_2\}Cl_2]$ complexes are either large enough so that restricted rotation does not occur or the nonequivalent *tert*-butyl groups give coincident chemical shifts.[33] Palladium complexes of *trans*-$[Pd\{t\text{-Bu}_2P(CH_2)_nPt\text{-Bu}_2\}Cl_2]_x$ (where $n = 10$ or 12 and $x = 1$ or 2) were produced in a manner similar to the platinum species and gave similar results during characterization.

In addition to platinum and palladium complexes, Shaw and co-workers also synthesized complexes of the type $[Ir\{(t\text{-Bu})_2P(CH_2)_xP(t\text{-Bu})_2\}(CO)Cl]$ (where $x = 9$, 10, or 12) by adding the bisphosphine ligand to a solution of chloroiridic acid and carbon monoxide in boiling ethanol to form *trans*-spanning monomers and dimers.[31,37] The X-ray crystal structures of [Ir-

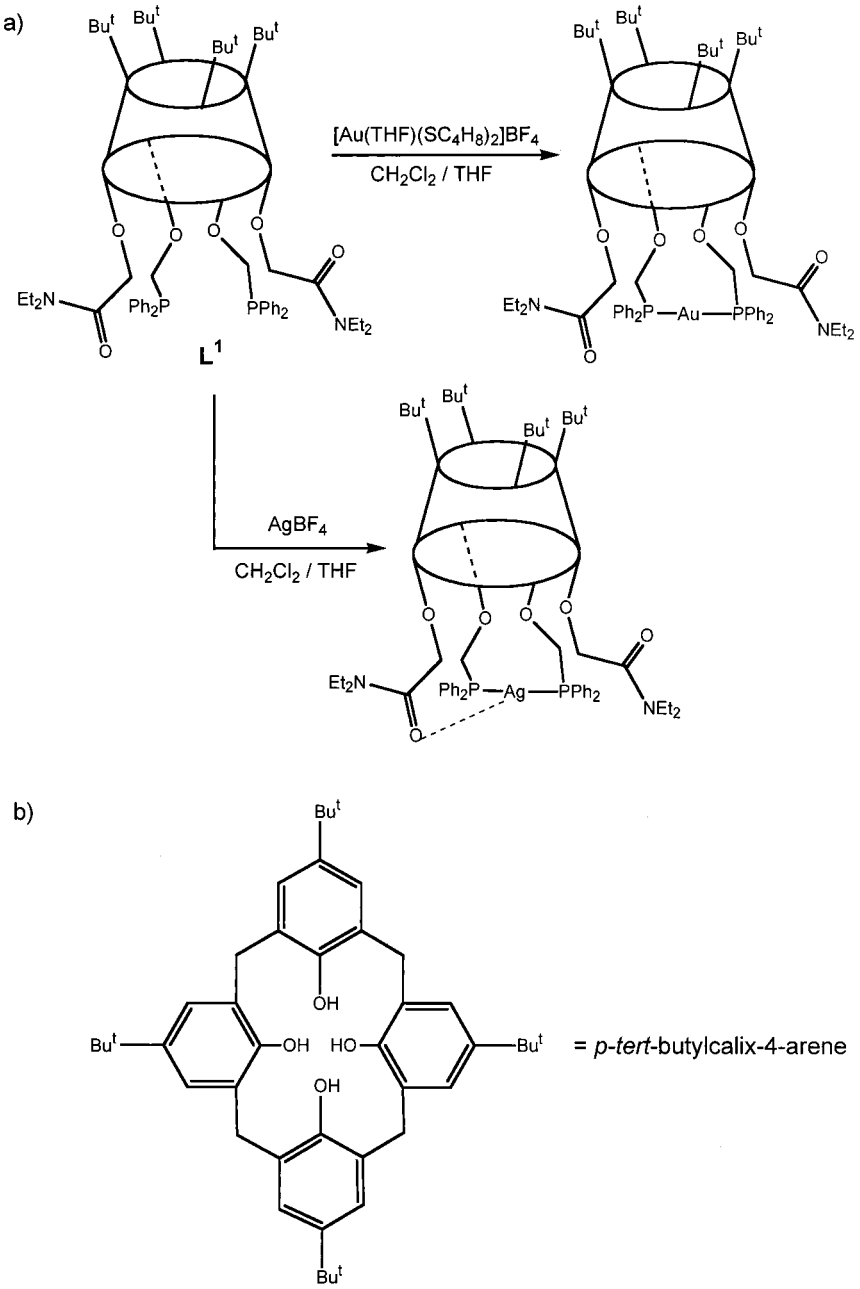


Figure 5. (a) Formation of *trans*-[Au(L^1)]BF_4 and *trans*-[Au(L^1)]BF_4.[28,29] (b) Skeletonal structure of a typical *p-tert*-butylcalix[4]arene ligand.[28]

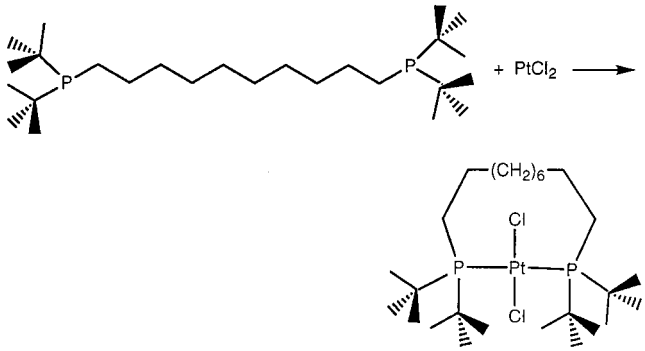


Figure 6. Preparation of *trans*-[Pt{(*t*-Bu)$_2$P(CH$_2$)$_{10}$P(*t*-Bu)$_2$}Cl$_2$].[31,33]

{*t*-Bu$_2$P(CH$_2$)$_{10}$P*t*-Bu$_2$}(CO)Cl], [Pt{*t*-Bu$_2$P(CH$_2$)$_{12}$P*t*-Bu$_2$}Cl$_2$], and [Rh{*t*-Bu$_2$P(CH$_2$)$_{10}$P*t*-Bu$_2$}(CO)Cl]$_2$ are identical in that either a chlorine or a carbonyl is gauche with respect to the sets of four *tert*-butyl groups on the *trans*-positioned phosphorus atoms.[37] In addition to the flexibility of the large rings (favorable internal entropy changes), the bulky *tert*-butyl groups hinder the phosphorus donor atoms from taking up mutual *cis*-positions but not mutual *trans*-positions (conformational effects), which effectively promote the *trans*-spanning chelate structure.[31]

While diphosphines of the type (*t*-Bu)$_2$P(CH$_2$)$_n$P(*t*-Bu)$_2$ (n = 9, 10, 12) give mono-, bi-, and trinuclear complexes [M{(*t*-Bu)$_2$P(CH$_2$)$_n$P(*t*-Bu$_2$)}Cl$_2$], the ligand (*t*-Bu)$_2$P(CH$_2$)$_8$P(*t*-Bu)$_2$ did not form any mononuclear complexes and was thought to be too small to span *trans*-positions.[36] This work again demonstrates that larger chelate rings form *trans*-spanning diphosphine

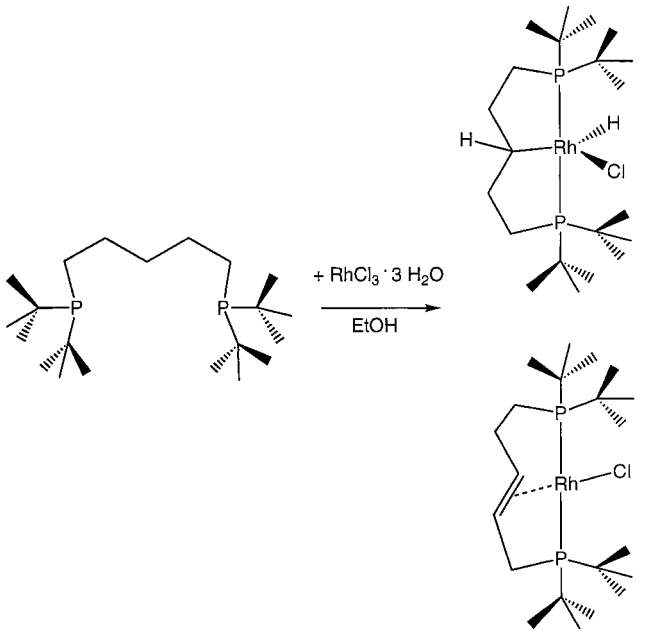


Figure 7. Reaction scheme for a mixture of rotamers: the cyclometalated [*Rh*{*t*-Bu)$_2$P(CH$_2$)$_2$*C*H(CH$_2$)$_2$P(*t*-Bu)$_2$}Cl] and the olefin complex, [Rh{(*t*-Bu)$_2$P(CH$_2$)$_2$CH=CHCH$_2$P(*t*-Bu)$_2$}Cl] from RhCl$_3$·3H$_2$O.[36]

complexes more effectively than small or intermediate chelate rings. The preparation of palladium or platinum chloride complexes utilizing the diphosphine ligands with chain lengths of $n = 5-7$ was investigated to further determine the effect of chain length on chelating ability. For example, the reaction of [Pd(NCPh)$_2$Cl$_2$] with (*t*-Bu)$_2$P(CH$_2$)$_5$P(*t*-Bu)$_2$ produced the 16-atom ring complex *trans*-[Pd{(*t*-Bu)$_2$P-(CH$_2$)$_5$P(*t*-Bu$_2$)$_2$}Cl$_2$] and the cyclometalated (and more soluble) complex [*Pd*{(*t*-Bu)$_2$*P*(CH$_2$)$_2$*C*H(CH$_2$)$_2$*P*(*t*-Bu)$_2$}Cl] (where *Pd* forms bonds with *P* and *C*) in yields of 62% and 12%, respectively. This mixture of products is typical of shorter alkyl chains ($n = 5-7$) using palladium and platinum.[36] The use of RhCl$_3$·3H$_2$O with the same diphosphine ligands, (*t*-Bu$_2$)P-(CH$_2$)$_n$P(*t*-Bu)$_2$ ($n = 5-7$), also gives a mixture of the binuclear 16-atom ring complex [Rh$_2${(*t*-Bu)$_2$P(CH$_2$)$_5$P-(*t*-Bu)$_2$}$_2$Cl$_4$H$_2$], which exists in solution as a mixture of two rotomers: the cyclometalated [*Rh*{(*t*-Bu)$_2$*P*-(CH$_2$)$_2$*C*H(CH$_2$)$_2$*P*(*t*-Bu)$_2$}Cl] (where *Rh* forms bonds with *P* and *C*) and a probable olefin complex [Rh{(*t*-Bu)$_2$P(CH$_2$)$_2$CH=CHCH$_2$P(*t*-Bu)$_2$}Cl] (Figure 7).[38] The reaction of hydrated iridium trichloride with (*t*-Bu)$_2$P-(CH$_2$)$_5$P(*t*-Bu)$_2$ also yields the dihydride [*Ir*{(*t*-Bu)$_2$-*P*(CH$_2$)$_2$*C*H(CH$_2$)$_2$*P*(*t*-Bu)$_2$}ClH] (where *Ir* forms bonds with *P* and *C*) and an unidentified complex.[29]

The preparation of palladium and platinum halide complexes with bidentate phosphine ligands, where a methyl group has been inserted into the middle of the polymethylene chain, (*t*-Bu)$_2$P(CH$_2$)$_2$CH(Me)-(CH$_2$)$_2$*P*(*t*-Bu)$_2$, was also studied.[40] While the reaction of [PdCl$_2$(NCPh)$_2$] with the methylated diphosphine produced the binuclear complex [Pd$_2${(*t*-Bu)$_2$P(CH$_2$)$_2$-CHMe(CH$_2$)$_2$P(*t*-Bu)$_2$}$_2$Cl$_4$] and no cyclometalated complexes, the reaction of [PtCl$_2$(NCPh)$_2$] with the same ligand resulted in an insoluble [Pt{(*t*-Bu)$_2$P-(CH$_2$)$_2$CHMe(CH$_2$)$_2$P(*t*-Bu)$_2$}$_x$Cl$_2$] complex as well as the volatile, cyclometalated [*Pt*{(*t*-Bu)$_2$*P*(CH$_2$)$_2$*C*Me-(CH$_2$)$_2$P(*t*-Bu)$_2$}Cl].[40] Iridium precursors also reacted with the methylated bidentate phosphine ligand, (*t*-Bu)$_2$P(CH$_2$)$_2$CH(Me)(CH$_2$)$_2$*P*(*t*-Bu)$_2$, to produce cyclometalated products. These studies[36,38-40] illustrate the potential problems of employing alkyl chain linkages in *trans*-spanning diphosphine complexes, namely, the unsystematic formation of mixtures of bi- and polymeric rings and cyclometalated products.

Although Shaw and co-workers initially believed that *tert*-butyl end groups were required for the formation of *trans*-spanning diphosphine complexes, later studies showed that phenyl end groups could be used but ligands containing phenyl groups had a tendency to form both *cis*- and *trans*-diphosphine species. The factors which influence the formation of *cis*- and *trans*-diphosphine isomers in platinum(II) complexes with long-chain bis(diphenylphosphine) alkanes (dpe, dph, dphp, dpo, dpn, dpd, dpu, dpdod, and dphd) were examined by Hill, McAuliffe, and co-workers.[41] The identity of the starting material was found to affect the *cis*- or *trans*-diphosphine geometry in the resulting complex. For example, *cis*-[Pt(diphenylphosphine ligand)Cl$_2$] complexes were formed from K$_2$PtCl$_4$, while Zeise's salt, K[PtCl$_3$(C$_2$H$_4$)], resulted in *trans*-geometries if the synthesis was performed under dilute conditions or *cis*-geometries if synthesized with an excess of phosphine ligand and/or with heating.[41] Molecular weight measurements on a number of the complexes indicated that the isolated product was generally a mixture of isomers in both monomeric and dimeric forms.

The *cis*-dimers were found to be the most stable isomers for the majority of the possible *cis*-complexes. The preferred ring sizes for the *cis*-chelated monomers were found to be 14- (dpu) and 19-membered (dphd) chelate rings.[41] The amount of *trans*-monomer increased with increasing chain length and reached a maximum with a chelate ring size of 15 members.[41] This trend can be correlated directly with ring contributions to the chemical shift (i.e., the difference between the coordination shift of similar bis(monophosphine) complexes (*trans*-[Pt{P(*n*-Bu)Ph$_2$}$_2$Cl$_2$]) and the coordination shift of the corresponding diphosphine complex, Δ_R). In *trans*-monomeric complexes, these ring contributions may be used as a measure of ring strain for these ligands.[41] Larger flexible chelate rings (19 members or above) appear to be unstable in the *trans*-configuration.

Further evidence that the identity of the metal complex starting material is important to the formation of *trans*-spanning diphosphine complexes was seen in the combination of dpo or dpd with nickel(II) halides (Cl^-, Br^-, or I^-) or thiocyanide. All of these highly colored precipitates were diamagnetic, indicating a square planar arrangement, and had an infrared spectrum that showed a single unsplit band for ν(Ni−X) and ν(Ni−P), indicating *trans*-stereochemistry.[42] While most of the nickel(II) halide complexes were insufficiently soluble for accurate molecular weight determinations, the two thiocyanate species gave molecular weights that were 70−80% higher than expected for monomers, which suggests that these complexes exist in solution predominantly as dimers, in equilibrium with some

monomer. The insolubility of the nickel halide derivatives indicated higher degrees of polymerization.[42]

Notably, cobalt(II) complexes with the same dpo and dpd ligands were found to be exclusively dimeric with tetrahedral coordination geometry,[42] and when the starting material $Rh(X)(PPh_3)_3$ was combined with dpo or dpd, the products [Rh(dpo or dpd)X-(PPh_3)] were obtained. The molecular weights of the rhodium compounds were all higher than those required for the [Rh(dpo or dpd)X(PPh_3)] monomers, but none were as high as the [Rh(dpo or dpd)X-$(PPh_3)]_2$ dimer values. Parish and Razzoki proposed that some dissociation (probably loss of PPh_3) occurred from the dimeric species.[42]

For complexes in which the basic coordination geometry of the metal is not in doubt (e.g., palladium(II) and platinum(II)), the chain length of the diphosphine ligand appears to be the most important factor in determining the coordination geometry. Polymeric species are favored by relatively short chains (ca. six linkage atoms). Cyclic dimers are found with 10−12 linkage atoms, and *trans*-spanning monomers result from long chains (ca. 16 links).[42] Palladium(II) complexes of dph, dpo, dpd, and dpdod are consistent with these predictions.[43] Generally, dph bridges two palladium atoms and forms polymeric complexes. The $[Pd(dph)Cl_2]$ complex demonstrates a ν(Pd−Cl) stretch at 357 cm^{-1} of a typical *trans*-arrangement and a solid-state reflectance spectrum with a broad absorption band at 24.5 kK, characteristic of square planar coordination about palladium.[43] $[Pd(dph)Br_2]$ has a similar structure; however, $[Pd(dph)I_2]$ has a low-energy absorption at 18.7 kK, indicating bridging iodine atoms, which result in a pentacoordinate palladium structure.[43]

While the dph ligand bridges two palladium atoms and forms polymeric complexes, both the dpo and dpd ligands bridge two palladium atoms forming dimeric 22- or 26-membered rings.[43] Molecular weight measurements and ^{31}P NMR spectra indicated that the dimers contained some dissociated monomeric units (approximately 2−10%). Finally, the dpdod ligand did not bridge metal centers; instead, it acted as a *trans*-chelating ligand, forming a monomeric complex containing a 15-membered ring. This demonstrated the effect of the length of the alkyl chain on the ability to form *trans*-spanned complexes.[43]

Rhodium(I) and iridium(I) centers affect the dehydrogenation of the alkane chain in the dph ligand forming metal olefin complexes of the type *trans*-[M(bdph)Cl].[44] Coordination of the olefin is confirmed by the resonance at 6.37 ppm, a shift upfield from that of the uncoordinated ligand in the ^{31}P NMR spectrum. The *trans*-chelating geometry is proposed as two of the protons in the 3 and 4 positions of the hexane chain of dph are able to overlap with the d_{xz} and d_{yz} orbitals of the metal complex (assuming a square planar configuration with the ligands occupying the xy plane) and the empty antibonding orbitals of the C−H bond. *trans*-Coordination of the diphosphine could facilitate the transfer of electrons from the metal with subsequent formation of a relatively unstable metal hydride species and the formation of a stable metal−olefin bond. Although no direct evidence is supplied for this dehydrogenation mechanism, it is noted that the iridium complex *trans*-[Ir(bdph)Cl] activates hydrogen reversibly at room temperature to form the *cis*-dihydride complex, *cis*-$[Ir(bdph)ClH_2]$.[44]

2,2′-Bis(diphenylphosphino)bibenzyl (bdpbz) and its arsenic analogue (bdabz) form monomeric complexes of rhodium(I), iridium(I), and platinum(II).[45] The Rh(I) complexes, *trans*-[Rh(bdpbz)(CO)Cl] and *trans*-$[Rh(bdpbz)(CO)_2]^+$, exhibit temperature-dependent ^1H NMR spectra, due to inversion of the nine-membered chelate ring (Figure 8). The estimated free energies of activation are 17.3 ± 0.3 kcal/mol at 93 °C for the neutral complex and 13.2 ± 0.5 kcal/mol at ca. −15 °C for the cationic complex.[45] Molecular models show that the nine-membered chelate ring formed by bridging bdpbz can take two possible conformations in which the carbon−carbon bond of the aliphatic chain is oriented at about 45° (A) or at about 90° (B) to the P−Rh−P axis. The conformers, both of which are chiral, are readily interconverted by rotation about the P−aromatic carbon bonds of the $P-C_6H_4$ units. Molecular models suggest that A is the more stable conformation, since *trans*-annular interactions between the hydrogen and the metal or the ligand appear less severe in A than in B. In contrast, the Pt(II) complex *cis*-[Pt(bdpbz)-$(CH_3)_2$] has an estimated free energy of activation of 16.1 ± 0.1 kcal/mol at 69 °C, and the Ir(I) complex, *trans*-[Ir(bdpbz)(CO)Cl], isomerizes in solution at room temperature by transferring a benzylic hydrogen atom to the metal and forming a metal−carbon σ-bonded complex, [Ir(bdpbz)(*C*O)ClH] (*C* is a metal-coordinated carbon atom).[45]

Like the dph ligand, the bdpbz ligand is dehydrogenated by various rhodium complexes, (Figure 9).[46] The initial rhodium complex is probably *trans*-spanned with the bdpbz ligand, but in a stepwise or simultaneous loss of hydrogen via mono- or dihydride intermediates, the rhodium(I) complex, $[Rh(Ph_2P(o\text{-}C_6H_4)CH{=}CH(o\text{-}C_6H_4)PPh_2)Cl]$, is produced. From this complex, bdpps can be displaced by treatment with NaCN.[47] While ligands bdpps, bdtps, and bdpbz seem to undergo *trans*-bidentate coordination and metalation with d^8 metals more readily than do the bulky *tert*-butyl or *o*-tolyl monophosphines of Shaw and colleagues,[47] these ligands have not been observed to form nickel(II)−carbon σ-bonded species. Although the driving force for metalation may be similar for both series of complexes (i.e., the C−H bonds are forced into the proximity of the metal atom by steric or geometric control), opposite effects resulted from increased bulk of these types of chelating ligands. Bennett and Clark[46] noted that bdtps undergoes metalation more slowly than bdpps, presumably as a consequence of steric hindrance by the bulky *o*-tolyl groups, whereas the ligands studied by Shaw and co-workers undergo metalation more rapidly as they become more sterically hindered.[47]

The factors governing *trans*-chelation in square planar complexes are still not clear. For flexible backbone chelates, Shaw proposed that the presence

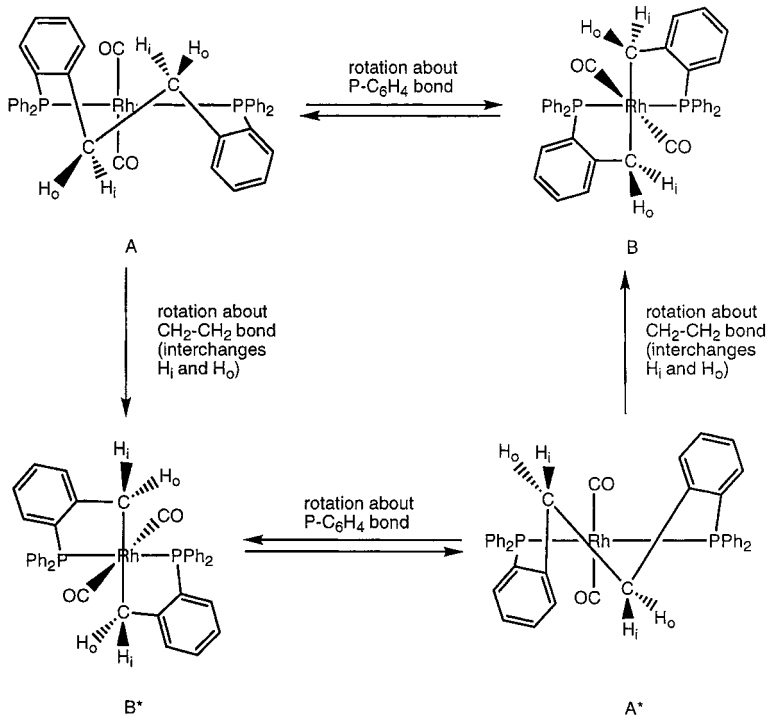


Figure 8. Inversion of *trans*-[Rh(bdpbz)$(CO)_2]^+$. A* and B* are mirror images of A and B; the outer (H_o) and inner (H_i) protons are interchanged by ring inversion.[45]

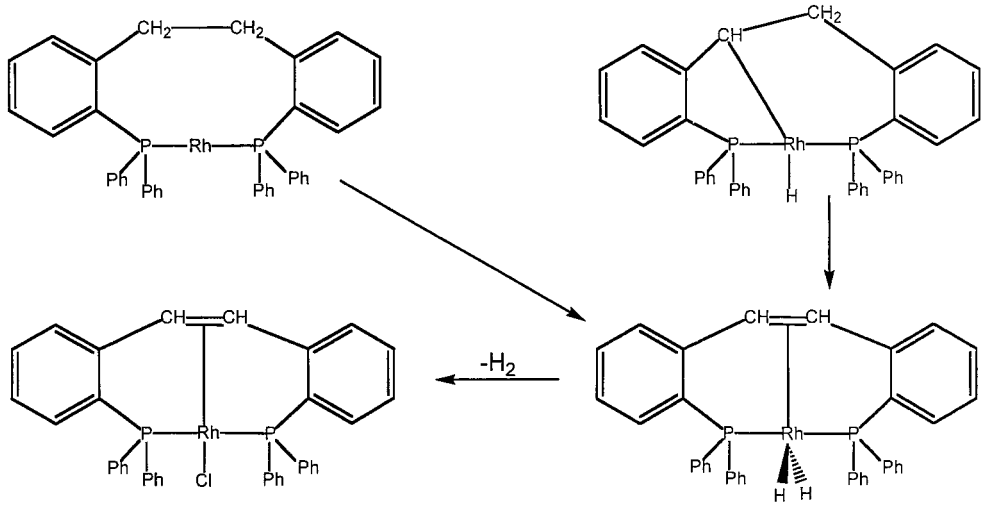


Figure 9. Generalized hydrogen abstraction reaction for *trans*-[Rh(bdpbz)$(CO)_2]^+$ and *trans*-[Rh(bdpbz)(CO)Cl]. Auxiliary chloride and carbonyl ligands are omitted for clarity.[46]

of bulky substituent groups on the donor atom produces favorable conformational effects and internal entropy changes which favor the formation of *trans*-chelated complexes.[48] However, studies by McAuliffe and co-workers showed that the presence of bulky substituent groups on the donor atoms may not be a prerequisite for *trans*-chelation. McAuliffe, Hill, and co-workers demonstrated that the choice of the complex precursor is crucial in determining the sterochemistry of platinum(II) complexes using the unsymmetrical bis(phosphine) ligands $Ph_2P(CH_2)_6P$-(Et)Ph and $Ph_2P(CH_2)_6PEt_2$. It was also noted that different products formed as a consequence of the length of the methylene chain as ligands of the type $Ph_2P(CH_2)_nPPh_2$, with $n = 8-10$ gave essentially dimeric species while when $n = 12$ *trans*-chelated monomers were formed.[48]

2. 2,11-Bis(diphenylphosphinomethyl)benzo[c]-phenanthrene (L1a) and Its Derivatives

The L1a ligand has been examined extensively in square planar complexes as this ligand has a tendency to attach itself to opposite corners of the square plane acting as a rigid "spacer". Initial studies involved the preparation of *trans*-$[M(L1a)X_2]$ complexes, where M = palladium(II), platinum(II), or nickel(II) and $X = Cl^-$, Br^-, I^-, or, for Ni complexes, NCS^-. These complexes are monomeric nonelectrolytes.[49]

Differences in the synthesis and characterization of transition-metal complexes utilizing L1a, monodentate *trans*-positioned (Ph_2PCH_2Ph) ligands, and *trans*-spanning alkyl ligands such as $(t\text{-Bu})_2P(CH_2)_nP$-$(t\text{-Bu})_2$ have been compared using Ni, Pt, and Pd

square planar complexes.[50] The reactions of NiX_2, $[PdX_2(PhCN)_2]$, $Na_2[MX_4]$, and other starting materials with the ligand L1a all give complexes of the type $[MX_2(L1a)]$, demonstrating complex formation independent of the identity of the starting material, a phenomenon which is not observed with alkyl *trans*-spanning diphosphine ligands. The use of the L1a ligand results in the yield of monomer of 65−98%, which is an improvement from yields of 20−30%, as reported for the *trans*-spanning ligands containing flexible alkyl chains of eight carbon atoms or more (i.e., $(t\text{-Bu})_2P(CH_2)_nP(t\text{-Bu})_2$).[50] Also, the L1a ligand reacts with nickel(II) to give, either exclusively or predominantly, mononuclear square planar complexes of the type *trans*-$[M(L1a)X_2]$, while $[Ni(Ph_2PCH_2Ph)_2X_2]$ complexes are found in both tetrahedral (paramagnetic) and square planar (diamagnetic) forms.[50] Complexes of the type $[Ni(Ph_2P(CH_2)_5PPh_2)X_2]$ (X = Br or I) have a tetrahedral structure. The fact that L1a forms only square planar complexes with nickel(II) provides confirmation for the hypothesis, based on studies with molecular models, that L1a does promote the formation of square planar complexes.[51]

The NMR, IR, and UV−vis spectra of *trans*-$[M(Ph_2PCH_2Ph)_2X_2]$ and *trans*-$[M(L1a)X_2]$ are similar in all regards. These complexes were characterized by ^1H NMR spectroscopy, where the *trans*-configuration of the L1a ligand was confirmed by a pseudotriplet in the region 3.5−5 ppm, arising from the $-CH_2-$ protons. These 1:2:1 triplets have been shown to be indicative of *trans*-configurations.[52] The number of ^{31}P NMR chemical shifts and coupling constants also confirm the *trans*-geometry, as exemplified in the NMR spectrum of $[Pt(L1a)Cl_2]$, which has a $^1J(^{195}P-^{31}P)$ value of 2578 Hz (as compared to 3731 and 2584 Hz for *cis*- and *trans*-$[Pt(Ph_2PCH_2Ph)_2Cl_2]$, respectively).[52] Finally, the coordination of the L1a ligand to the metal center often results in a strong-to-medium IR band at ca. 1100 cm^{-1}, which Venanzi and co-workers used as an empirical indication of the coordination of the L1a ligand.[50]

The ligand L1a has also been used to prepare the mononuclear, square planar complexes *trans*-$[M(L1a)(CO)X]$ and *trans*-$[M(CH_3CN)(L1a)(CO)][BF_4]$ (M = Rh, Ir; X = Cl^-, Br^-, I^-, and NCS^-). The complex $[Rh(L1a)(CO)Cl]$ was synthesized from L1a and $[Rh_2(CO)_4Cl_2]$. Subsequent treatment of *trans*-$[Rh(L1a)(CO)Cl]$ with Ag^+ in CH_3CN gave *trans*-$[Rh(CH_3CN)(L1a)(CO)]^+$. The combination of *trans*-$[Rh(L1a)(CO)Cl]$ with added NaBr, NaI, or NH_4NCS in acetone/ethanol solutions formed the corresponding *trans*-$[Rh(L1a)(CO)X]$ species.[53] Notably, in these complexes the methylene hydrogens generally give a set of four triplets which can be assigned to the spin system *AMXX′M′A′*. As this pattern is observed only when the other ligands in the square planar complexes are different, it is presumed that the orientations of H_a and H_m are restricted in such a way that they experience different average shielding effects.[53] These complexes have a tendency to form adducts with CO, O_2, and SO_2 to a lesser degree than the analogous L = $2PPh_3$ complexes.[53]

The X-ray crystal structures of $[Rh(L1a)(CO)Cl]$, $[Pd(L1a)Cl_2]\cdot C_6H_5CN$, $[Ir(L1a)(CO)Cl]$, and $[Pt(L1a)Cl_2]$ have been determined.[54,55] In both the rhodium and palladium complexes, the metal atom is four-coordinate with a distorted square planar configuration. The distortion in both of the crystal structures tends toward tetrahedral coordination, i.e., the P−M−P, Cl−Rh−C, and Cl−Pd−Cl angles are less than 180°, and the planes defined by (P, Rh, and Cl) and (P, Pd, and L1a) make angles of 12.4° and 13.3° in the rhodium and palladium complexes, respectively. The P−M−P bond angles in $[Rh(L1a)(CO)Cl]$ and $[Pd(L1a)Cl_2]\cdot C_6H_5CN$ are 174.7(1)° and 175.7(1)°, respectively.

Strong out-of-plane deformations of the benzophenanthrene ligand backbone in $[Rh(L1a)(CO)Cl]$ and $[Pd(L1a)Cl_2]\cdot C_6H_5CN$ are a consequence of severe overcrowding.[54] In both the rhodium and palladium complexes, the benzophenanthrene ligand backbone deformation is the only distortion of the molecule that seriously breaks the molecular symmetry with respect to a mirror plane perpendicular to the P−P axis. This distortion is characteristic of compounds containing the benzophenanthrene ligand backbone and is caused by the interaction of H(1) and H(12).[54] The mirror symmetry extends to the phenyl rings bound to the P atoms as they are nearly eclipsed. The shortest M···H contact is 2.85 Å for Rh−H or Pd−H, while the shortest Cl···H contacts range from 2.70 to 2.90 Å. Notably, the basic geometric structure of the complexes of the type [M(L1)ClX] (M = Rh, Pd, Ir, Pt) is unaffected when changing L from CO to Cl or changing the identity of the metal atom.

Continuing an examination of the X-ray structures of complexes containing the L1a ligands, it is noted that compounds which have P(1)−M−P(2) angles near 180° include the following: *trans*-$[Pd(L1a)Cl_2]$ (176.7(1)°), *trans*-$[Rh(L1a)(CO)Cl]$ (174.7(1)°), $[Au(L1a)Cl]$ (175.7(1)°), and *trans*-$[Pt(L1a)ClH]$ (176.2(1)°), among others.[56] In this set of complexes, the L1a ligand has a conformation in which the two methylene−phosphorus bonds C(19)−P(1) and C(20)−P(2) are oriented in the same direction with respect to the tetranuclear part of the ligand. In a second set of compounds containing the L1a ligand, the P(1)−M−P(2) angles are less than 150°. This set of complexes includes $[Cu(L1a)Cl]$ (131.9(1)°), $[Ag(L1a)Cl]$ (140.77(1)°), and $[Hg(L1a)Cl_2]$ (125.6(3)°).[56] In these latter complexes, the two methylene−phosphorus bonds point in opposite directions with respect to the tetranuclear part of the ligand.

The notably smaller P(1)−M−P(2) bond angles of the second set of complexes indicate that while L1a forms mainly *trans*-spanned coordination complexes, *cis*-mononuclear complexes can also be formed. Reaction of L1a with $[Pt(1,5\text{-}C_8H_{12})_2]$ and subsequent treatments with HCl(g), $Ag[BF_4]$, and CH_2CHCO_2Me yields the *cis*-mononuclear complex of platinum(II).[56] The X-ray crystal structure of *cis*-$[Pt(L1a)Cl_2]$ shows a major distortion in the square planar coordination of the P(1)−Pt−P(2) angle of 104.8(1)°.[56] In this complex, the two methylene−phosphorus bonds point in opposite directions, even though the dihedral angle is small and the phenyl groups are almost

eclipsed. The valence angles of L1a ligand indicate that the molecule is very strained, with the two phenyl groups (one on each phosphorus) lying parallel to each other, separated by ca. 3.2−3.3 Å. These nonbonded intramolecular C···H contacts between phenyl rings are often important in stabilizing the conformations of aromatic species.[56]

The ^{31}P NMR spectrum of the *cis*-[Pt(L1a)Cl_2] complex confirms the *cis*-geometry, demonstrating a ^1J(Pt,P) of 3611 Hz.[56] Homonuclear decoupling experiments show that there are two magnetically distinct phenyl rings. One phenyl group has protons with *o*-, *m*-, and *p*- chemical shift values which are considered normal for a phenyl group coordinated to a phosphorus atom (7.5−8.0 ppm) and a second set of phenyl group protons which are moved to higher fields (6.7−7.0 ppm). This second set of phenyl group protons are also indicative of aromatic rings which are constrained so that one ring is placed above the other.[56] The higher field resonances indicate that *cis*-[Pt(L1a)Cl_2] retains its conformation even in solution state. Infrared bands at 315 and 290 cm^{-1} which are characteristic of *cis*-coordination were also observed. In light of these studies, Venanzi and co-workers proposed that the *cis*-arrangement of phosphorus donors in *cis*-[Pt(L1a)Cl_2] is a result of the pathway by which the complex is formed.[56]

To study the steric and electronic effects of the L1a ligand, the phosphine substituents were modified to include Ph, *m*-PhCH_3, *p*-PhOCH_3, *m*-PhCF_3, C_6H_{11}, and *t*-Bu groups in complexes of the type [M(L1)X_2] (M = Ni, Pd, and Pt; X = Cl^- or NCS^-).[57] Assuming the *trans*-conformation, each of the H, H′, R, and R′ groups are chemically and magnetically nonequivalent. During the rapid 'fanlike' movement of the benzo[*c*]phenanthrene linkage across the top of [M(L1)-X_2] complexes, the H and H′ (and R and R′) experience a time-averaged environment, whereas for square planar complexes of the form *trans*-[M(L1)-ClH], H and H′ are always different due to the differing local anisotropic effects of Cl^- and H^-.

For complexes of the form *trans*-[M(L1b)X_2] (M = Ni, Pd, Pt; X = Cl^- or NCS^-), the *tert*-butyl signals provide a simple probe through which the fanlike motion of L1b is monitored.[57] Temperature-dependent NMR spectroscopy shows that three distinct phases exist. At high temperature, the rapid motion of the organic backbone leads to averaging of the proton environment with signal coalescence occurring at 293 K for *trans*-[Ni(L1b)$(NCS)_2$], 323 K for *trans*-[Pd(L1b)Cl_2], and >333 K for *trans*-[Pt(L1b)Cl_2]. The second, lower temperature phase shows slower benzo-[*c*]phenanthrene motion as demonstrated by the *tert*-butyl resonances which appear as two 1:1 triplets. The third phase shows a new motional process in which either the R or R′ resonance (but only one) begins to broaden as the temperature is further reduced. For *trans*-[Pt(L1b)Cl_2], the ^{1}H NMR spectrum at 213 K consists of four *tert*-butyl resonances in a ratio of 1:3:1:1, where each retains the triplet structure, confirming the *trans*-orientation of the phosphorus atoms. Venanzi and co-workers suggest that this NMR pattern is caused by the relatively slow motion about the P,C-bond of the two P−*t*-Bu units.[57]

Ligand substitution in square planar complexes generally occurs by an associative mechanism in which both direct ligand addition and solvent-assisted ligand addition contribute. Steric hindrance suppresses the usual associative ligand substitution reactions and may favor a dissociative mechanism. Venanzi and co-workers investigated the effect of the *trans*-spanning phosphine linkage, L1d, in comparison with two *trans*-positioned monodentate phosphines (L = PEt_3 and P(*m*-PhCF_3)$(CH_2Ph)_2$) in complexes of *trans*-[Pt(2 L or L1d)RX] (R = H or Me; X = Cl^- or 4-PADA), where the incoming group was either 4-PADA or I^-.[58] The steric effects were small, and all reactions took place according to the usual two-term rate law indicative of an associative reaction.

Notably, when either the L1d ligand or two {P(*m*-PhCF_3)(CH_2Ph)} (2L) ligands is used in *trans*-[Pt-(2 L or L1d)RX], the reaction pathway for associative ligand substitution reactions is similar. For the *trans*-[Pt(2L or L1d)RX] complexes, the direct reaction path (entering nucleophile) is dominant and the solvent or dissociative path is slow or immeasurable.[58] It is proposed that in addition to steric considerations, the solvent-assisted mechanism may be hindered by incomplete solvation in the region of the phenyl rings since steric blocking caused by the L1d and {P(*m*-PhCF_3)(CH_2Ph)} ligands is not sufficient to hinder the attack on the complex by an entering nucleophile. The reactivity order for the hydride complexes is *trans*-[Pt$(PEt_3)_2$XH] < *trans*-[Pt{P(*m*-PhCF_3)$(CH_2$-Ph)}XH] < *trans*-[Pt(L1d)XH]. With the corresponding methyl complexes, there is some retardation of the ligand substitution rate by L1d, but this has been attributed to an interaction between the methyl group and the hydrocarbon moiety of L1d which subsequently influences the fluxional behavior of the *trans*-spanning ligand.[58]

The key step in many catalytic cycles is the insertion of an alkene into a M−H bond, producing a *cis*-configured product. Normally, it is proposed that the metal complex must have a *cis*-configuration before alkene insertion occurs. To test this hypothesis, complexes of the type *trans*-[Pt(L1a)YH] (Y = Cl^-, I^-, NO_3^-, acetone, CH_3CN, CO, or PPh_3) were prepared. The *trans* → *cis* isomerization reaction represents a sterically hindered reaction pathway for these complexes. Notably, the insertion of ethene into *trans*-[Pt(acetone)(L1a)H]$^+$ was observed, leading to the formation of *trans*-[Pt(acetone)(L1a)(Et)]$^+$; however, complexes of the form *trans*-[Pt(L1e)XY] (X = H or Me; Y = OMe, OCHO, CO_2H, and BH_4) showed a tendency to form hydrido-bridged binuclear complexes, such as *trans*-[(L1d)HPt(μ-H)PtH(L1d)]$^+$, despite the bulk of ligand L1d and the length of the chelate ring.[59]

In further reactivity studies, L1a was compared with other phosphine ligands (L = 2 PPh_3, 2 PPh_2-CH_3, and $Ph_2PCH_2CH_2PPh_2$) in 1,1-reductive elimination reactions involving *cis*- and *trans*-[Pd(L or L1a)$(CH_3)_2$] complexes.[60] Unlike the other phosphine-containing complexes, *trans*-[Pd(L1a)$(CH_3)_2$] failed to

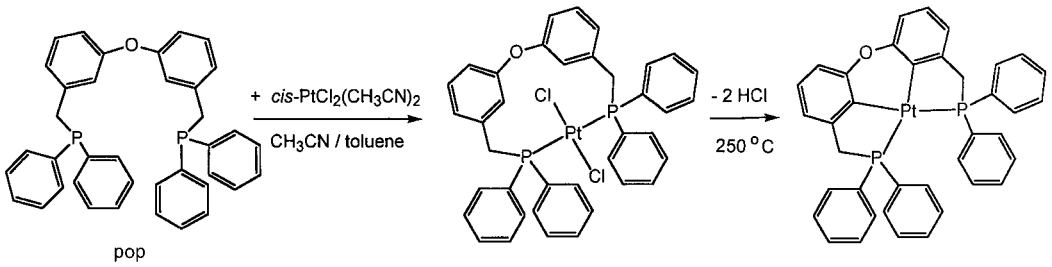


Figure 10. Synthesis of *trans*-[Pt(pop)Cl_2] and thermal dehydrohalogenation to [Pt(pop-2H)].[61]

undergo reductive elimination of ethane at extreme temperatures and lengthy reaction times, implying the *trans* → *cis* conversion as a necessary step for reactivity. However, this complex did add CD_3I to rapidly produce CD_3CH_3.

3. Ether Linkages

While the use of L1a is well established, Kapoor and co-workers used the more easily synthesized bidentate ligand, pop, to investigate the effect of the restricted backbone flexibility on the *trans*-coordination of diphosphine ligands.[27] Notably, comparison of the L1a and pop ligands shows that the addition of two freely rotating bonds in pop relative to L1a is not detrimental to *trans*-chelation. The pop ligand forms monomeric, *trans*-spanning square planar complexes *trans*-[M(pop)X_2] (where M = Ni, Pd, Pt, or Rh and X = Cl^-, Br^-, I^-, N_3^-, NCS^-, CN^- or NO_3^-) as well as *trans*-[Pt(pop)ClH], *trans*-[Pt(pop)BrH], and *trans*-[Rh(pop)(CO)Cl].[27]

Reaction of NiX_2 and PdX_2 with pop resulted in strictly *trans*-configured square planar complexes of the type *trans*-[M_2(pop)X], establishing the thermodynamic preference for the *trans*-coordination of the pop ligand. In contrast, with Pt(II), which measures the kinetic preference for *trans*-chelation,[27] the nature of the starting material, the solvent, reaction time, reaction stoichiometry, and temperature strongly affected the relative quantities of the product. For example, $Pt_2(C_2H_4)_2Cl_4$ or $Pt(C_6H_5CN)_2Cl_2$ resulted in good yields of dimer, while other starting materials (e.g., $Pt(CH_3CN)_2Cl_2$) gave the most efficient synthesis of *trans*-[Pt(pop)Cl_2] monomer. Both *cis*- and *trans*-polymers were unstable in solution, isomerizing to the thermodynamically stable *trans*-monomer and other polymers.[27] The formation of monomer and dimer products with the pop ligand could be explained by changes in the entropy of internal rotation; however, Kapoor and co-workers propose that the entropy contribution is probably outweighed by the strain energy of the transition state in the case of the *cis*-[Pt(pop)Cl_2] monomer.[27] Polymeric species have been observed with substitutionally inert metal centers: *trans*-[Pt(pop)Cl_2]$_2$ and *cis*-[Pt(pop)Cl_2]$_n$ (where *n* has a mean value of 4−5). Finally, the reaction of $Rh_2(CO)_4Cl_2$ with pop gave both a soluble fraction, identified as *trans*-[Rh(pop)(CO)Cl], and an insoluble fraction, postulated as the polymeric species *trans*-[Rh(pop)(CO)Cl]$_x$.

The complex *trans*-[Pt(pop)Cl_2] undergoes thermolysis at ca. 250 °C with the evolution of 2 mol of HCl to form a doubly cyclometalated complex, [3,3′-oxybis[((diphenylphosphino)methyl)benzene]ato(2-)-C^2,$C^{2'}$,P,P']platinum(II), Pt(pop-2H) (Figure 10).[61] The solid-state mechanism for this reaction was probed using optical microscopy, NMR spectroscopy, heated X-ray powder diffraction, and thermal analysis techniques. On heating, an unstable melt is formed, and this melt allows for more molecular motion than a true solid-state reaction. Deuterium-labeling studies showed that during thermolysis, approximately one hydrogen displaced the *ortho*-deuterium of the perdeuterated phosphino phenyl groups. This rearrangement was interpreted as a sequence of cyclometalation steps that led to a four-membered metalacycle (i.e., a four-membered ring composed of Pt, P, and two adjacent carbon atoms from the phenyl ring of the phosphine ligand).[61]

Another flexible diphosphine ligand, bis{3-bis(3-trifluoromethylphenyl)phosphinomethyl]phenyl}-ether, (m-CF_3)$_4$pop), also formed monomeric square planar complexes of the type *trans*-[M((m-CF_3)$_4$pop)-X_2], where M = Ni, Pd, or Pt and X = Cl^- or M = Ni and X = NCS^-.[62] Reaction of (m-CF_3)$_4$pop with MCl_2 or $Ni(NCS)_2$ yielded the complexes *trans*-[M((m-CF_3)$_4$pop)X_2]. The hydride complex *trans*-[Pt((m-CF_3)$_4$pop)ClH] was obtained by ligand exchange from *trans*-[Pt(PPh_3)$_2$ClH] with retention of configuration. The use of the (m-CF_3)$_4$pop ligand yielded more soluble complexes than the use of the pop ligand.[62]

Alcock, Brown, and Jeffery reacted tetracarbonylrhodium dichloride with the *p*-phosphinoether ligands $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ to obtain the *trans*-spanning complexes *trans*-[Rh{$Ph_2P(CH_2CH_2O)_nCH_2$-CH_2PPh_2}(CO)Cl], where n = 1−3.[63] These complexes showed no tendency to undergo oxidative addition with O_2, H_2, or CO, although they did react reversibly with SO_2, giving a five-coordinate adduct, or with HCl, giving a six-coordinate adduct. Notably, these complexes could be reacted with Ag^+ to form a bond between the ether oxygen and the rhodium metal center. The crystal structures of the symmetrically bridged ether species *trans*-[Rh{$PPh_2(CH_2)_2$(OCH_2-CH_2)PPh_2}(CO)]$^+$ (where *O* is coordinated to the central Rh, Figure 11) as well as the hydrogen-bonded ether complex *trans*-[Rh(H_2O){$PPh_2(CH_2)_2$-(OCH_2CH_2)$_3PPh_2$}(CO)]$^+$ (where the ether linkages are hydrogen-bonded to the aqua ligand on Rh(I)) are reported.[63,64] The geometries of both species are nearly square planar. In the former complex, the P(1)−Rh−P(2) bond angle of 165.9(1)° is indicative of an in-plane distortion, while in the latter complex, the P(1)−Rh−P(2) angle of 174.3(1)° indicates less strain.[64] For the *trans*-[Rh{$PPh_2(CH_2)_2$(OCH_2CH_2)-PPh_2}(CO)]$^+$ complex, the dominant feature governing the structure of the bicyclic ring system is the

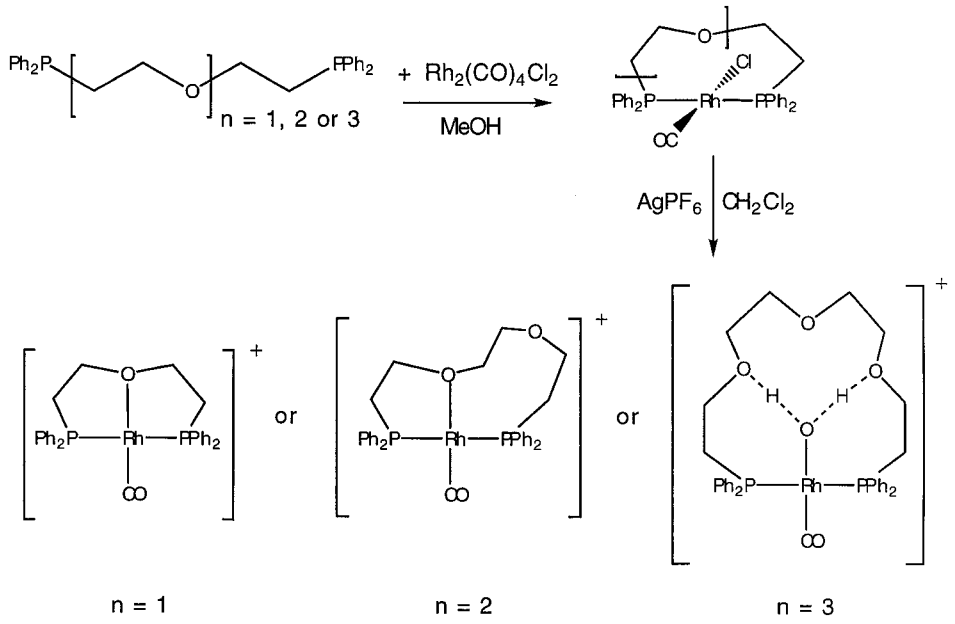


Figure 11. Syntheses of rhodium complexes with *trans*-chelating phosphinoether ligands.[63,64]

staggered conformation about the C−C bonds. The ligand binds asymmetrically, but the observed eclipsed conformations indicate that the torsion barrier about the Rh−P bond must be low. For the *trans*-[Rh(H_2O)-{$PPh_2(CH_2)_2(OCH_2CH_2)_3PPh_2$}(CO)]$^+$ complex, the phosphine ligand functions as a bidentate donor, where the water molecule which is coordinated to the metal center hydrogen bonds to the terminal ether oxygens. The central ether oxygen is almost pyramidal, whereas the terminal ether oxygens are essentially trigonal sp^2 hybridized. The resultant symmetry in the diphosphine chain gives two equal energy conformations with a very low torsion barrier between them.[64] Notably, ether complexes of group VIIIB metals are relatively rare; thus, these examples illustrate the importance of chelation in stabilizing otherwise weak metal−ligand interactions.

Timmer and Thewissen obtained similar products as they investigated the reaction between Rh(acac)-(COD), CO, and several *trans*-spanning phosphinoether linkages $Ph_2P-(o\text{-}C_6H_4O((CH_2)_2O)_2\text{-}o\text{-}C_6H_4)$-$PPh_2$, $Ph_2P-(o\text{-}C_6H_4O((CH_2)_3O)_2\text{-}o\text{-}C_6H_4)PPh_2$, and $Me(Ph)P-(o\text{-}C_6H_4O((CH_2)_2O)_2\text{-}o\text{-}C_6H_4)P(Ph)Me$ to form η^3-*trans*-[Rh(CO)(phosphinoether)]$^+$ complexes.[65] Like Alcock and co-workers, the authors propose that these phosphinoether ligands are bound to the rhodium metal center through the *trans*-phosphorus atoms as well as the ether oxygen (which is *trans* to the carbonyl) based on infrared and NMR spectroscopic studies.[65]

When $n = 1$, the $PPh_2(CH_2)_2(OCH_2CH_2)_nPPh_2$ ligand coordinated to rhodium(I) as a terdentate ligand by donating both phosphorus atoms and the oxygen atom.[64] When $n = 3$, the ligand formed a loose chain with a tightly held water molecule encapsulated in the large ring.[64] When $n = 2$, the *trans*-[Rh-{$PPh_2(CH_2)_2(OCH_2CH_2)_2PPh_2$}($CH_3CH_2OH$)(CO)]$^+$ complex contained an encapsulated ethanol molecule; however, this molecule was much less firmly bonded to the rhodium center.[66] The crystal structure of the $n = 2$ complex was essentially square planar, with P(1)−Rh−P(2) = 178.6°, and the angles about phosphorus were close to tetrahedral, implying that this molecule had the least strain of the series.[66] Attempts to form the neutral *trans*-[Rh{$PPh_2(CH_2)_2(OCH_2CH_2)$-PPh_2}Cl(CO)] resulted in dimer formation.

In addition to forming *trans*-spanning diphosphine complexes by coordinating the phosphine ligand twice to the metal, Hill and co-workers used the method of Bailar and co-workers[67] to synthesize *trans*-spanning complexes by initially coordinating quadridentate ligands to the metal center and then dissociating two M−L bonds to form *trans*-bidentate species.[68] The ligand dpdo readily forms [Ni(dpdo)X_2] complexes (where X = Cl^-, Br^-, I^-, or NCS^-). While these complexes exhibit solid-state electronic reflectance spectra typical of pseudotetrahedral species, the solution-state spectra indicate a square planar structure.[68] Additionally, the room-temperature magnetic moments reflect a change in the solid-state structure from pseudotetrahedral (Cl^-, 3.25 μ_B) to square planar (I^-, 0.0 μ_B) geometry with the bromo complex representing a spin-crossover point.[68]

The crystal structure of *trans*-[Ni(dpdo)$(NCS)_2$] has a P(1)−Ni−P(2) angle that is close to linear 175.9-(1)°, while replacement of the NCS^- by the more sterically demanding iodide ligand leads to a more drastic distortion from square planar geometry with a P(1)−Ni−P(2) angle of 162.1(4)° and an I(1)−Ni−I(2) angle of 145.3(3)°.[68] For *trans*-[Ni(dpdo)I_2], the shortest I···C(phenyl) interligand separation is 3.60 Å, ca. 0.3 Å less than the sum of the van der Waals radii, where the steric crowding might result in the above distortion from square planar geometry.[68] Finally, the diamagnetic, square planar structure [Ni(H_2O)$_2$(dpdo)][BF_4]$_2$ was tentatively suggested to contain a *trans*-chelating dpdo ligand. However, both the electronic reflectance and room-temperature magnetic moment of the related complex [Ni(H_2O)$_4$(dpdo)-Cl_2] indicated an octahedral geometry with coordination of the ether oxygens.[68] It was suggested that

the latter complex has either a *cis*- or *trans*-geometry with dpdo acting as a quadridentate ligand in the solid state, but in halocarbon solutions, the ether linkages are released, forming bidentate *trans*-diphosphine complexes.

Sacconi[69,70] and co-workers plus Hill[71,72] and co-workers compared the use of dpdo with dpo as both ligands have eight intermediate atoms between the two phosphorus donors.[71] A comparison of nickel complexes of dpdo and dpo indicated that the backbone flexibility of the noncoordinating ether functionality is different from that of the noncoordinating methylene groups.[69−71] The [Ni(dpo)X_2] complexes ($X = Cl^-$, Br^-, I^-) exhibit electronic spectra which are indicative of a high-spin, pseudotetrahedral geometry in both the solid state and in methylene chloride solution,[69,71] while the [Ni(dpo)$(NCS)_2$] complex has a solid-state reflectance spectrum indicative of planar geometry.[71] At room temperature, the solid-state magnetic moments of the dpo complexes exhibit a spin-crossover between high-spin, pseudotetrahedral geometries ([Ni(dpo)Br_2], 3.11 μ_B and [Ni(dpo)I_2], 3.24 μ_B) and square planar species ([Ni(dpo)Cl_2], 2.48 μ_B).[71] The latter complex may represent a spin-crossover point, since there is no evidence in the electronic spectra for any diamagnetic, planar isomer. The [Ni(dpo)$(NCS)_2$] complex is diamagnetic.[71] The low solubility of the chloro and bromo complexes prevented reliable molecular weight determinations; however, the [Ni(dpo)I_2] species was consistent with a dimeric structure, and it is likely that the former complexes are also pseudotetrahedral dimers.[71]

The complexes [Ni(dpdo)X_2], where $X = Cl^-$ or Br^-, are pseudotetrahedral in the solid state but square planar in CH_2Cl_2. For $X = I^-$ or NCS^-, a monomeric metal geometry tending toward square planar is present in both the solid state and in solution.[69] The electronic spectrum of [Ni(dpdo)I_2] is red shifted with respect to the corresponding band found in some low-spin, square planar Ni(monodentate phosphine)$_2I_2$ complexes giving some difficulty in assigning the geometry of the complex; however, the crystal structure of this complex indicates a tetracoordinated structure, intermediate between square planar and tetrahedral structures.[69,70] For the Ni(dpdo)I_2 complex, the I(1)−Ni−I(2) angle is 143.5(0.3)° and the P(1)−Ni−P(2) angle is 162.1(0.4)°.[69,70] Notably, the analogous Ni(dpo)I_2 complex is high spin with an electronic spectrum characteristic of tetrahedral geometry.[70]

Continuing studies with the dpdo ligand have lead to monomeric *cis*- and *trans*-complexes of the formula [M(dpdo)X_2], where M = Pd and $X = Cl^-$, Br^-, I^-, or NCS^- or M = Pt and $X = Cl^-$ or I^-.[72] The syntheses of the *cis*-[Pd(dpdo)X_2] complexes were carried out in polar solvents, while *trans*-isomers were prepared in less polar solvents. The *cis*-[Pt(dpdo)X_2] complexes were prepared from $K_2[PtCl_4]$, while *trans*-isomers were prepared from Zeise's salt, $K[PtCl_3(C_2H_4)]$.[72] The NMR spectrum of *trans*-[Pt(dpdo)X_2] ($X = Cl^-$ or Br^-) is complex, but it is consistent with a monomeric formulation in chloroform. The P(1)−Pd−P(2) and I(1)−Pd−I(2) bond angles are 164.9(1)° and 146.8(1)°, respectively,[72] slightly larger than for analogous [Ni(dpdo)I_2] complexes, as expected due to the larger metal radius of palladium.[69] In contrast to [Ni(dpdo)I_2], where more than one conformer of the chelate backbone was observed, only one conformation exists for [Pd(dpdo)I_2] and the $O-CH_2-CH_2-O$ torsion angle of 69° supports the staggered conformation. Notably, the formation of both *cis*- and *trans*-species with an 11-membered chelate ring had not been observed previously.[72]

The reaction of $Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$ with $PdCl_2$ yields an equilibrium mixture of cyclic polymers and monomers with the empirical formula [Pd$\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\}Cl_2$].[73] Both *cis*- and *trans*-coordination geometries are observed, with the *trans*-form being more abundant. At low solute concentrations, monomers are favored over polymers, but as the concentration increases, the amount of polymer increases as well. Additionally, as the temperature is increased, the *cis* → *trans* isomerization equilibrium constant increases while both the dimerization equilibrium constant and polymerization equilibrium constants decrease (i.e., as the equilibrium shifts toward monomers, the *trans*-configuration is favored).[73]

The modeled concentration and temperature dependencies of the equilibrium constants are consistent with the thermodynamics of *cis* → *trans* isomerization and reversible step polymerization. Models with two equilibrium constants for step polymerization sufficiently described the solution equilibrium of [Pd$\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\}Cl_2$] when the *cis* → *trans* equilibrium constant was calculated to be 1.8 ± 0.3 at 308 K (2.3 ± 0.3 at 331 K) in acetonitrile-d_3.[73] This *cis* → *trans* equilibrium constant was smaller than that observed for the model monodentate complex [Pd$\{Ph_2P(CH_2CH_2O)_2CH_3)\}_2Cl_2$], 6.6 ± 0.5 at 308 K (9.5 ± 0.4 at 331 K).[73]

Interestingly, the dimerization equilibrium constant for [Pd$\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\}Cl_2$] was nearly an order of magnitude smaller than the polymerization equilibrium constant (Figure 12).[73] This surprising difference indicated the step polymerization is more easily accomplished than the polymerization of the monomer. The authors propose that this difference is due to the ether oxygens as they are oriented to readily recoordinate to the palladium center as the diphenylphosphine group dissociates.[73] The hemilabile coordination of the ether oxygen in the monomer would hold the diphenylphosphino group in the proximity of the palladium center and favor coordination of the phosphine to the same palladium to reform the monomer rather than coordination to a new metal center to form dimers. In the polymer, the ether oxygens are not close enough to the palladium center to recoordinate when the phosphine disphenylphosphine group dissociates, and thus, the equilibrium constant is greater.

To understand the effects of the length and nature of the chelate chain on the *cis* → *trans* and monomer/oligomer equilibria in long-chain bis(phosphine) complexes, quantitative $^{31}P(^1H)$ NMR studies in $CDCl_3$ solutions of [Pd$\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\}Cl_2]_n$ (n = 3, 4, 5) and [Pd$\{Ph_2P(CH_2)_{12}PPh_2\}Cl_2$] were modeled using a single *cis* → *trans* isomerization

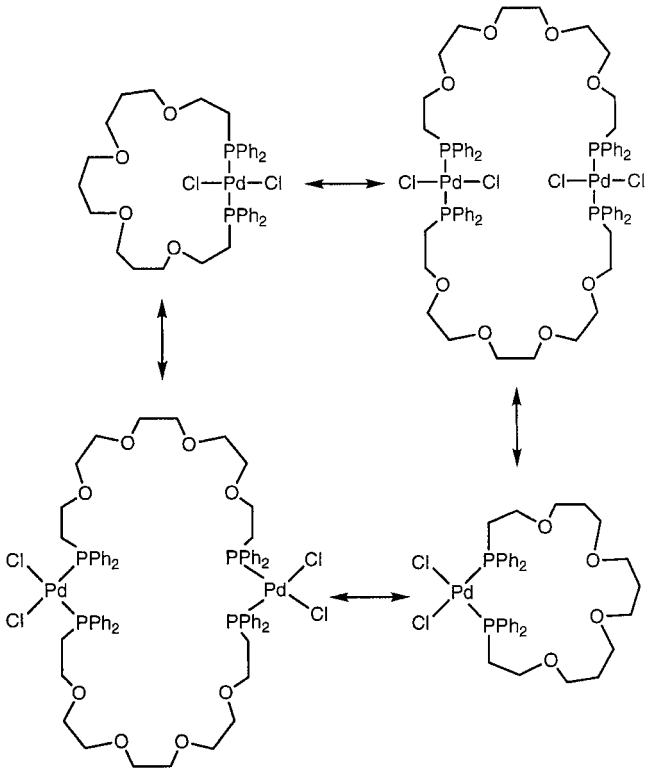


Figure 12. Proposed polymerization−isomerization equilibria in solutions of [Pd{$Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-*P*,*P*′}$Cl_2$].[73]

equilibrium and two-step polymerization (dimerization, oligomerization) equilibria.[74] The equilibrium constant for *cis* → *trans* isomerization of all the complexes increases with temperature. This is due to the fact that the maximization of solute−solution disorder favors the *trans*-isomers in solvents with low polarities such as $CDCl_3$. The *cis* → *trans* equilibrium constants for the larger spanning linkages (15-membered rings or greater; ether or alkyl) are similar in magnitude and are significantly larger than that of 12-membered ether ring. This suggests that when *trans*-coordinated, the smaller ligands are more strained than the larger ligands.[74]

Both the dimerization and oligomerization equilibrium constants for the metallacrown ethers, $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$, increase as *n* increases; however, the dimerization equilibrium constants of the metallacrown ethers are much smaller than the oligomerization equilibrium constants.[63] In contrast, the dimerization and oligomerization equilibrum constants for [Pd{$Ph_2P(CH_2)_{12}PPh_2$}Cl_2] are nearly identical and are significantly larger than those of the metallacrown ethers. These differences indicate that both dimerization and oligomerization are more favorable with alkylene chains than with polyether chains.[74] Finally, the very different dimerization constants for the metallacrown ethers and [Pd{$Ph_2P(CH_2)_{12}PPh_2$}Cl_2] and the similar rates for formation for the *trans*-metallocrown ether monomer and *trans*-oligomers suggest that the isomerization and dimerization reactions have a common rate-determining step that involves cleavage of a palladium−phosphorus bond.

In addition to ether linkages containing oxygen, thioethers may also be used as *trans*-spanning phosphine linkages. The ligand PSP behaves as a tridentate ligand forming the pentacoordinated complex, Ni(PSP)I_2; however, this complex partially dissociates in solution to form a planar species.[75] All of the corresponding halonickel(II) complexes with the PC_4P, PC_5P, and POP ligands are high spin and thus were assigned to distorted tetrahedral structures. The results indicated that the complexes Ni(PC_nP)X_2 with $n = 4$ or 5 are similar to the $(PPh_3)_2$ analogues, i.e., high spin in the solid state and in solution. The PC_nP derivatives with $n = 2$ or 3 are all planar in the solid state.[76] Notably, the POP analogue was pseudotetrahedral with the oxygen atom unbonded; comparisons with the sulfur-containing analogue may indicate a difference in the donor power of oxygen over sulfur; however, it was determined that the structural variations are more dependent on chain length than on electronic factors.[76] Presumably, increasing the chain length causes significant overcrowding around the nickel atoms such that the square planar configuration becomes unfavorable.

4. Acetylenic Linkages

Generally, the rigidity of the acetylenic linkages aids in the formation of larger ring complexes. The complex *trans*-[Rh{*t*-$Bu_2P(CH_2)_4C{\equiv}C(CH_2)_4P$*t*-$Bu_2$}Cl(CO)] was shown, by X-ray crystallography, to have a square planar geometry with a distance from the metal to the center of the acetylenic function of 5.25 Å, clearly demonstrating no bonding interactions (Figure 13).[77,78] While the acetylenic functionality provides rigidity to the *trans*-spanning chelate ring, there is no evidence for the conformational disorder found in many of the saturated long-chain diphosphine ligands.[77]

Shortening the diphosphine chain gives the monomeric complex *trans*-[Rh{*t*-$Bu_2P(CH_2)_2$*CH*=*CH*$(CH_2)_2$-P*t*-Bu_2}Cl] (where the olefin functionality, −CH=CH−, is coordinated) after metalation of the carbon−hydrogen bond and reductive elimination. This second structure has a *transoid* arrangement about the coordinated alkene fragment in the solid state; however, ^{31}P NMR spectroscopy showed that a minor component (ca. 8%), assigned to the *cisoid* arrangement, was present in solution. In the *cisoid* complex, the metal−carbon bond lengths averaged 2.15(1) Å. The ring configuration oriented the carbon−carbon olefin vector at 76° to the phosphorus−phosphorus vector in the *cisoid* complex, whereas the plane of the carbon−carbon bond of the alkyne in the *transoid* complex was oriented within 1° of the phosphorus−phosphorus vector.[78]

The variation in the Rh−P bond length between the sterically unstrained 26-membered ring of *trans*-[Rh{*t*-$Bu_2P(CH_2)_4C{\equiv}C(CH_2)_4P$*t*-$Bu_2$}Cl(CO)] (2.348(3) Å) and the 13-membered ring in *trans*-[Rh{*t*-$Bu_2P(CH_2)_2$*CH*=*CH*$(CH_2)_2$P*t*-Bu_2}Cl]) (2.316(3) Å) was attributed to intraannular strain phenomenon.[78] The smaller steric effects of the phenyl substituents on the phosphorus atoms and the different carbon chain connecting the two phosphorus atoms resulted in a smaller Rh−P bond distance for the [Rh{(*o*-Ph)$_2$$PC_6$-$H_5$*CH*=*CH*$C_6H_4P$(*o*-Ph)$_2$}Cl] complex (2.283(2) Å), even though it also contains a 13-membered ring.[77]

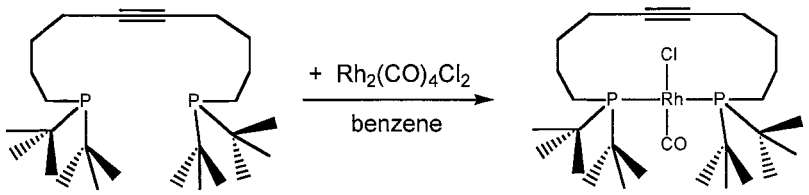


Figure 13. Synthesis of *trans*-[Rh{*t*-$Bu_2P(CH_2)_4C{\equiv}C(CH_2)_4P$*t*-$Bu_2$}(CO)Cl].[77,78]

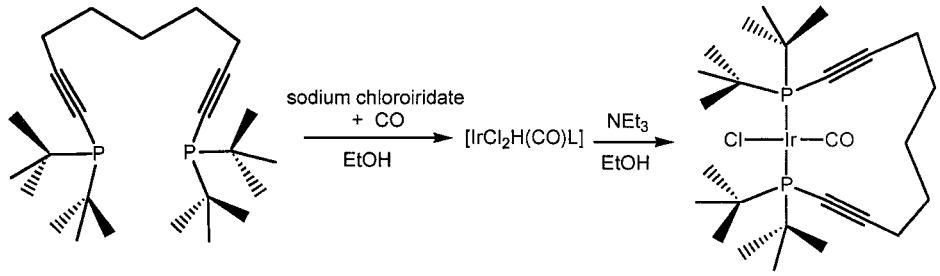


Figure 14. Synthesis of *trans*-[Ir{*t*-$Bu_2PC{\equiv}C(CH_2)_5C{\equiv}CP$*t*-$Bu_2$}(CO)Cl].[79]

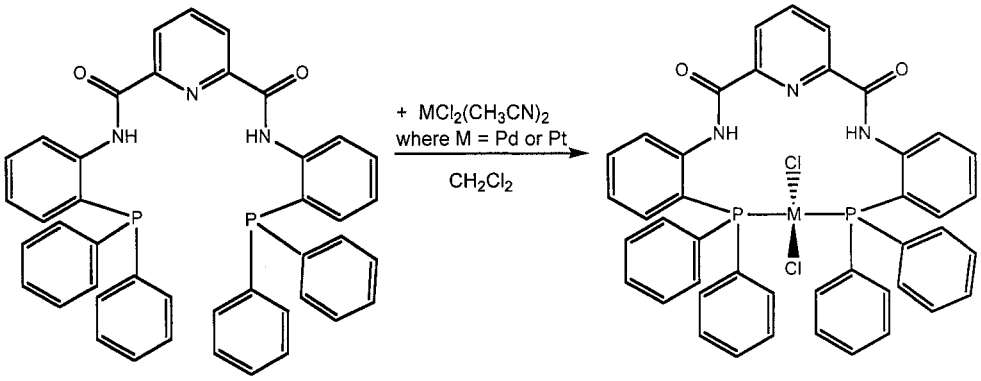


Figure 15. Synthesis of *trans*-[M{bis[*N*,*N*′-(2-diphenylphosphino)phenyl]-2,6-pyridinedicarboxamide}Cl_2].[80]

The diacetylene diphosphine complex *trans*-[Ir{*t*-$Bu_2PC{\equiv}C(CH_2)_5C{\equiv}CP$*t*-$Bu_2$}Cl(CO)] demonstrates an X-ray crystal structure in which two rotamers are present: one in which the CO is in a gauche position with respect to the four *tert*-butyl groups and one in which Cl^- is gauche to the *tert*-butyl groups.[79] In the ^{31}P NMR spectrum, only one rotamer is present, presumably the one in which the Cl^- is gauche, as this rotamer could be stabilized by the adjacent C≡C and C≡O functionalities. As observed for the alkyl-spanning phosphine complexes, the identity of the starting material controls product formation: while sodium chloroiridate produces *trans*-[Ir{*t*-Bu_2−$PC{\equiv}C(CH_2)_5C{\equiv}CP$*t*-$Bu_2$}Cl(CO)] (Figure 14), sodium bromoiridate gives only the binuclear species, [Ir{*t*-Bu_2−$PC{\equiv}C(CH_2)_5C{\equiv}CP$*t*-$Bu_2$}Br(CO)]$_2$, i.e., no molecular species were detected.[79] Presumably, the bromide ligand is sufficiently large to prevent the diphosphine from spanning the *trans*-positions of the mononuclear complex.

Finally, the behavior of the diacetylenic diphosphine is very different toward iridium than toward platinum and palladium. No mononuclear or binuclear species could be detected with either platinum or palladium.[79] Reaction of {*t*-Bu_2−$PC{\equiv}C(CH_2)_5C{\equiv}CP$*t*-$Bu_2$} with [Pt(*t*-BuCN)$_2Cl_2$] resulted in the formation of a hexameric species [Pt{*t*-Bu_2−$PC{\equiv}C(CH_2)_5C{\equiv}CP$*t*-$Bu_2$}$Cl_2$]$_6$, which was suggested to contain a 72-membered ring. Reaction of {*t*-Bu_2−$PC{\equiv}C(CH_2)_5C{\equiv}CP$*t*-$Bu_2$} with [Pd(PhCN)$_2Cl_2$] generated heptameric species. Shaw, Mason, and co-workers suggest that the chlorocarbonyl iridium behaves differently from Pt or Pd due to a nonvalence interaction between the carbonyl group and the acetylene, which holds the chain in a particular conformation and promotes the formation of a monomeric species (or in the case of bromide a binuclear species).[79]

5. Other Spanning Linkages

Feringa and co-workers synthesized new *trans*-spanning square planar complexes by reaction of bis[*N*,*N*′-(2-diphenylphosphino)phenyl]-2,6-pyridinedicarboxamide with either Pt(CH_3CN)$_2Cl_2$ or Pd(CH_3-CN)$_2Cl_2$ (Figure 15).[80] The ^{31}P NMR of the platinum complex *trans*-[Pt{bis[*N*,*N*′-(2-diphenylphosphino)-phenyl]-2,6-pyridinedicarboxamide}Cl_2] shows a single resonance at δ 15.4 ppm with a ^2J coupling to ^{195}Pt of 2457 Hz, consistent with a *trans*-geometry.[80] In the ^1H NMR spectrum of the platinum complex, the absorption of the amide protons is shifted to δ 11.05 ppm. This is assigned to the hydrogen bonding of the amide protons to chlorine. The crystal structure of the platinum complex has a distorted square planar coordination, where the P(1)−Pt−P(2) angle of 174.43-(5)° and the Cl(1)−Pt−Cl(2) angle of 172.25(5)° differ significantly from 180°.[80] Finally, the analogous palladium complex *trans*-[Pd{bis[*N*,*N*′-(2-diphenyl-phosphino)phenyl]-2,6-pyridinedicarboxamide}Cl_2] also demonstrates one singlet in the ^{31}P NMR spectrum

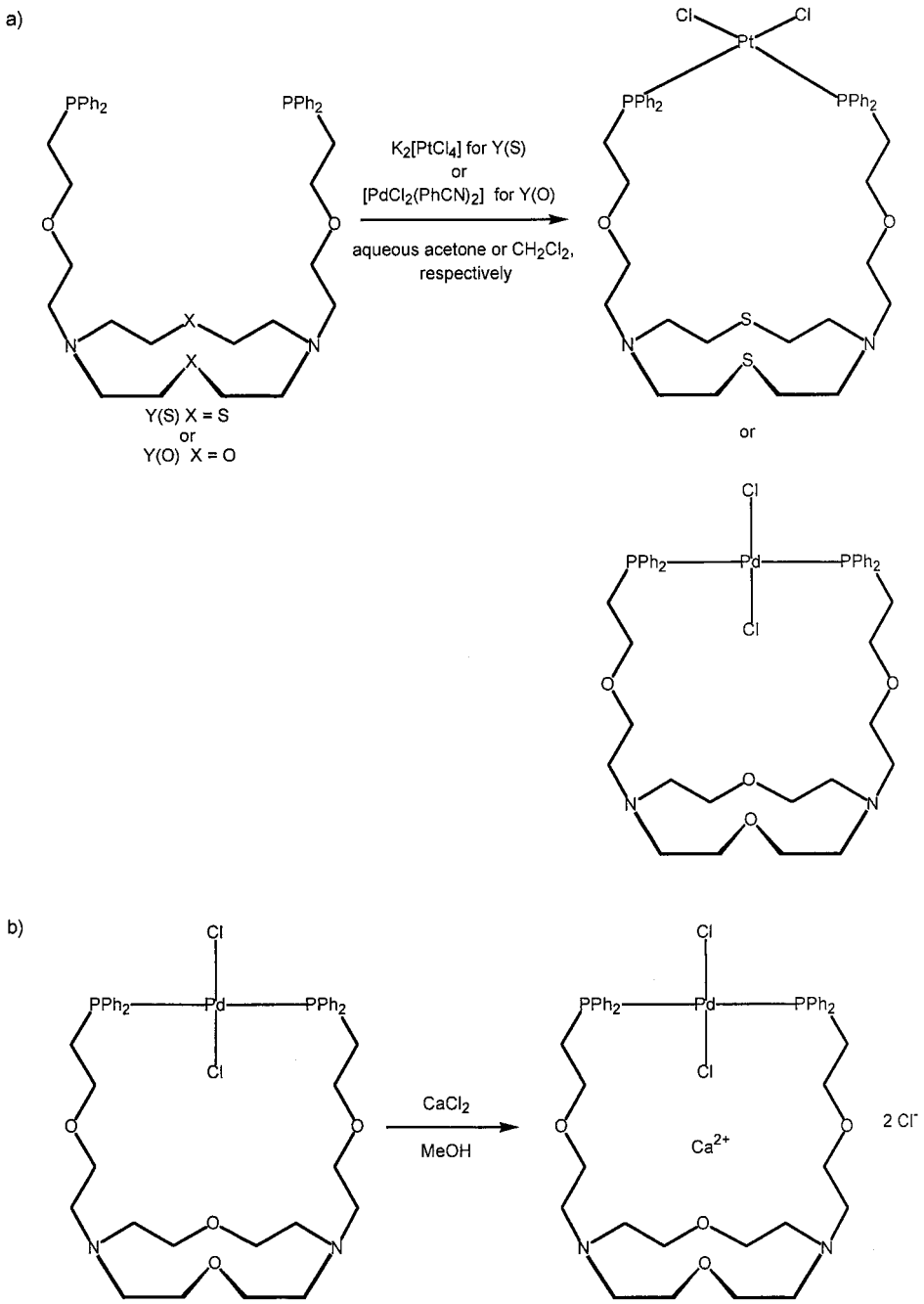


Figure 16. (a) Synthesis of *cis*-[$PtCl_2${Y(S)}] and *trans*-[$PdCl_2${Y(O)}]. (b) Coordination of Ca^{2+} by *trans*-[$PdCl_2${Y(O)}].[81]

at δ 19.4 ppm, and the amine proton was observed at δ 11.11 ppm.[80]

trans-Spanning complexes containing a heterotopic ligand that combines a subunit containing a "soft" binding site with a subunit containing a "hard" binding site were investigated by Lehn, Parker, and co-workers.[81] Reaction of $PdCl_2(PhCN)_2$ with Y(O) (see Figure 16) in dichloromethane yields the stable *trans*-isomer as the major species in solution.[81] Notably, the reaction of Y(O) with other starting materials and solvents, e.g., K_2PtCl_4 in aqueous acetone, results in the selective formation of *cis*-[$PtCl_2${Y(O)}]. Also, the replacement of the oxygen donor atoms in Y(O) with sulfur donor atoms (Y(S)) results in the nonselective coordination to both soft S_2 and P_2 binding sites giving dipalladium dichloride complexes (especially with [$PdCl_2(PhCN)_2$]).[81]

Ligand Y(O) binds Ca^{2+} in methanol to form a 1:1 complex which then reacts with $PdCl_2(PhCN)_2$ to form a heterodinuclear complex.[81] Ligands Y(O) and Y(S) also permit the formation of heterodinuclear compexes via the stepwise complexation, i.e., Y(O) react with [$PdCl_2(PhCN)_2$] in CH_2Cl_2 to generate *trans*-[$PdCl_2${Y(O)}], which in turn reacts with excess $Cu(ClO_4)_2$ in methanol to precipitate a heterodinuclear metal complex. The authors propose that this final complex has a *cis*-diphosphine coordination based on infrared spectroscopy ($\upsilon_{(PdCl)}$ 313 and 278 cm^{-1}).[81]

Other families of preformed ligands capable of forming square planar complexes have recently been investigated by Matt[28−30] and co-workers. These ligand families have been developed from α-cyclodextrins and calix[4]arenes and other pocket or

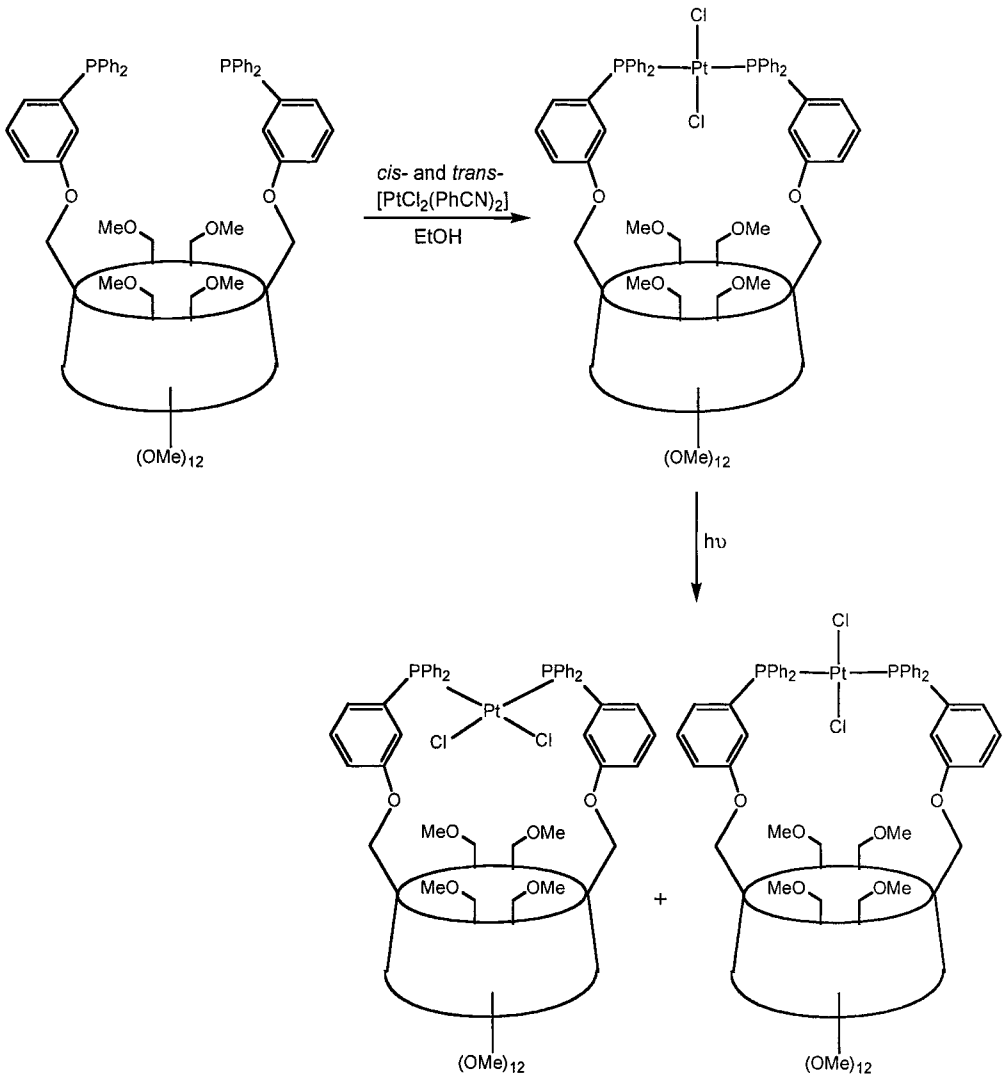


Figure 17. Synthesis of *trans*- and *cis*-complexes of [$PtCl_2${(3-$C_6H_4PPh_2$)$_2$-α-cyclodextrin}].[30]

cavity-forming rigid structures. Matt and co-workers treated (3-$C_6H_4PPh_2$)$_2$-α-cyclodextrin with [$PtCl_2$-($PhCN)_2$] (a mixture of *cis*- and *trans*-isomeric complex) to exclusively yield the *trans-P,P′*-chelated complex.[30] Further exposure of this complex to sunlight resulted in a 65:35 mixture of monomeric *trans*- and *cis*-isomers, respectively (see Figure 17). A similar reaction with [$PdCl_2(PhCN)_2$] and (3-C_6H_4-PPh_2)$_2$-α-cyclodextrin resulted in a rapidly interconverting mixture of *trans*- and *cis*-complexes before exposure to light. Reaction of the (3-$C_6H_4PPh_2$)$_2$-α-cyclodextrin ligand with [{$Rh(CO)_2Cl$}$_2$] also results in a square planar, *trans*-phoshine complex, *trans*-[Rh(CO)Cl{(3-$C_6H_4PPh_2$)$_2$-α-cyclodextrin}]. This latter complex was found to be an active catalyst in the conversion of oct-1-ene to the corresponding aldehydes. Both high conversions (>99%) and chemoselectivities (70:20 linear:branched aldehyde products) were obtained after 18 h in aqueous methanol. While this high turnover frequency (70 h^{-1}) compares well with standard nonionic hydroformylation catalysts, the low solubility of this rhodium complex remains a potential problem.[30]

Matt and co-workers also reported the synthesis of platinum and palladium square planar complexes using (Ph_2P)$_2$-substituted calix[4]arenes.[29] Treatment of [$PtH(THF)(PPh_3)_2$]$^+$ with the phosphine-substituted calix[4]arene ligand results in the formation of *trans*-[PtH{(Ph_2P)$_2$-substituted calix[4]arene}(PPh_3)]$^+$ quantitatively. The ^{31}P NMR spectroscopy unambiguously established the *trans*-spanning behavior of the diphosphine ligand as well as the presence of two types of phosphorus atoms. The authors proposed that the PPh_3 ligand positioned *trans* to the hydride ligand forces the Pt−H bond to point inside the calixarene cavity due to the upfield chemical shift (ca. 1.3 ppm upfield) of the hydride with respect to the analogous [$PtH(PPh_3)_3$]$^+$ ion.[29] Notably, this platinum complex was also inert to *trans* → *cis* isomerization, indicating the stability of the inclusion complex.

In an effort to synthesize complexes with larger metallo fragments inside the calix[4]arene pocket, Matt and co-workers also synthesized *trans*-[Pd-{(Ph_2P)$_2$-substituted calix[4]arene}(CH_3)(py)]$^+$ by reaction of [$Pd(COD)(CH_3)(THF)$]BF_4 with the substituted calix[4]arene followed by treatment with pyridine.[29] Again, two-dimensional NOESY spectra indicate that the methyl hydrogen atoms lie in close proximity to the phenolic CH bonds of the two phosphorus-stubstitued phenoxy rings. As the bulky pyridine ligand does not allow the pyridine−Pd−CH_3 fragment to rotate freely, the methyl group is firmly

locked inside the cavity, demonstrating the ability of these *trans*-spanning diphosphine ligands to entrap or confine molecular fragments bound to transition-metal ions.

In another work, Matt and co-workers investigated the reaction of L^1 (defined in Figure 5) with *trans*-[$PtClH(PPh_3)_2$] to form the *trans*-[$PtClH(L^1)$] complex.[28] Vapor-phase osmometry showed the complex to be clearly monomeric.[82] The two-dimensional ROESY (rotating frame Overhauser enhancement spectroscopy) spectrum indicated that the hydrido ligand was in close proximity to each OCH_2 group of the pendant arms as well as the axial H atoms of the bridging $C_6H_2CH_2C_6H_2$ groups. This suggests that the hydrido ligand is directed into the mouth of the calixarene cavity defined by the four phenolic oxygen atoms.[28] Subsequent treatment of the *trans*-[$PtClH(L^1)$] complex with $AgBF_4$ leads to the loss of the chloride ligand and bonding of one of the amide carbonyl groups. This binding effectively displaces the other carbonyl group away from the metal center, making the regions immediately above and below the platinum center very different; such asymmetry is rare in the platinum chemistries. The authors regard the P_2O ligand as a hemispherical strap of the metal center across the mouth of the calixarene.[28] Variable temperature ^1H NMR spectra did not indicate amide interconversions in the temperature range −30 to +80 °C in $C_2H_2Cl_4$. Finally, the coordinated amide moiety is ready displaced by PPh_3 or 4,4′-bipyridine yielding either monomeric or binuclear complexes, respectively.

Reaction of *trans*-[$PtHCl(PPh_3)_2$] with substituted calix[4]arenes, L^1−L^4 (where calix[4]arene = 5,11,17,23-tetra-*tert*-butyl-25,27-di-RCH_2O-26,28-bis(diphenylphosphinomethyoxy)calix[4]arene and R = $C(O)NEt_2$, L^1; C(O)OEt, L^2; (*R*)-C(O)NHCH(CH_3)Ph, L^3; or CH_2OMe, L^4) resulted in mixtures of complexes of the general formula *trans*-[$PtH(PPh_3)L^i$]Cl (type A) and *trans*-[$PtClHL^i$] (type B).[28] The type A:B ratio was found to depend on the coordinating ability of the R groups as they act as internal solvent molecules in promoting the substitution of the PPh_3 ligand. When strong donating groups were used (e.g., L^1 or L^2), complexes of *trans*-[$PtClHL^i$] were favored; however, with L^4, the reaction led selectively to *trans*-[$PtH(PPh_3)L^4$] with no *trans*-[$PtClHL^4$] being formed. In the case of L^3, the type A complexes could be converted to type B.[28]

Reaction of the carbonyl-coordinated complex *trans*-[$PtH(L^1)$]BF_4 with dimethyl acetylenedicarboxylate gave the insertion product *trans-P,P′*-[$Pt(MeO_2CC{=}CHCO_2Me)L^1$]$BF_4$, where the two amides competed for coordination.[28] Additionally, the carbonyl-coordinated complex *trans*-[$PtH(L^1)$]BF_4 was found to readily react with tetracyanoethylene (tcne) to yield the platinum(0) complex, *trans*-[$Pt(tcne)L^1$]. The NMR spectra of this latter complex suggested fast flipping of the coordination plane between amides. In contrast to the [$Pt(MeO_2CC{=}CHCO_2Me)L^1$]$BF_4$ complex, strong tridentate P_2O coordination was found with the rhodium carbonyl complexes [$Rh(CO)(L^1$ or $L^3)$]BF_4 obtained from [$Rh(CO)_2(THF)_2$]BF_4 and the corresponding diphosphino-substituted calix[4]arenes.[28]

C. Preformed Trigonal Bipyramidal or Square Pyramidal Complexes

Five-coordinate species containing *trans*-spanning diphosphines are relatively unstable when compared to the four-coordinate species, especially for complexes of L1a and Rh(I) or Ir(I).[53] While the complex *trans*-[$Ir(PPh_3)_2(CO)Cl$] reacts with CO giving [$Ir(PPh_3)_2(CO)_2Cl$], the addition of a second CO ligand to [Ir(L1a)(CO)Cl] yields [$Ir(L1a)(CO)_2Cl$]; however, attempts to isolate [$Ir(L1a)(CO)_2Cl$] led to the recovery of starting material. (The reaction of CO and *trans*-[$Rh(CH_3CN)$(L1a)(CO)] also results in recovery of the starting material.[53]) On addition of CO to solutions of *trans*-[$Ir(CH_3CN)$(L1a)(CO)]$^+$, a red color forms (thought to be [$Ir(L1a)(CO)_2$]) before becoming colorless. The colorless product is thought to be [$Ir(L1a)(CO)_3$]$^+$, but this complex also decomposes readily both in solution and in the solid state.[53] Venanzi and co-workers postulate that the decomposition of [$Ir(L1a)(CO)_3$]$^+$ is more complex than simple loss of CO, but they do not speculate on the actual product.

Reactions of *trans*-[Ir(L1a)(CO)Cl] with excess SO_2 gave one product by NMR analysis; however, this product, assumed to be *trans*-[$Ir(L1a)(CO)Cl(SO_2)$], could not be isolated and reverted to starting material reversibly. The analogous *trans*-[Rh(L1a)(CO)Cl] complex did not react with SO_2 or with PPh_3 (presumably due to unfavorable steric interactions).[53]

The five-coordinate, mononuclear complexes [$M(L1a)(CO)_3$], where M = Fe or Ru, were also prepared and assigned to trigonal bipyramidal structures.[83] The iron complex was best prepared by the thermal reaction of [$Fe(CO)_3(C_8H_8)$] with L1a in 1,2-dimethylcyclohexane; however, other methods (including photochemical methods) have also been successful. The ruthenium complex was more difficult to synthesize than the iron complex; photochemical activation was required as other methods to prepare [$Ru(L1)(CO)_3$] were unsuccessful.[83]

Complexes of the type [$Fe(CO)_3(L)_2$] (L = PR_3 or $P(OR)_3$) have been assigned to trigonal bipyramidal structures with apical phosphorus atoms.[84] The infrared spectra of [$M(L1a)(CO)_3$] (M = Fe or Ru) complexes were assigned in analogy to these complexes.[83] The chemical shift values of the ^{31}P NMR spectra were consistent with the *trans*-diphosphine arrangements. The ^1H NMR spectra of the benzylic protons for [$Fe(L1a)(CO)_3$] appear as 'filled-up' doublets, while for [$Ru(L1a)(CO)_3$], 'triplets' were observed. This latter pattern is consistent with the expected large value of $^2J(P,P)$, arising from the presence of a transition metal in the second row and *trans*-phosphorus atoms.[52,85]

The *trans*-[Ru(L1a)Cl(NO)] complex was prepared from the phosphine exchange reaction of *trans*-[$Ru(PPh_3)_2Cl(NO)$].[86] This complex was subsequently used to prepare *trans*-[Ru(L1a)(CO)Cl(NO)], *trans*-[$Ru(Ph_2PCH_2Ph)_2(CO)Cl(NO)$], and *trans*-[Ru(L1a)Cl(1-ethyl-3,5,8-trioxa-4-phosphabicyclo(2.2.2)octane)(NO)]. The crystal structure of *trans*-[Ru(L1a)(CO)Cl(NO)] shows the coordination about the metal to be a distorted trigonal bipyramid with the phosphorus atoms in axial positions (the P(1)−M−P(2) angle = 167.4(1)°). The trigonal bipyramidal struc-

ture is distorted toward a square pyramidal structure having the N−O ligand at the apex.[86] The Ru−N−O angle of 142.8(7)° indicates that the NO ligand can be considered to be NO^-, and hence, the ruthenium center was assigned a +2 oxidation state. The formation of *trans*-[Ru(L1a)(CO)Cl(NO)] was thus described as the addition of NO to the d^8-ruthenium(0) complex [Ru(L1a)(CO)Cl]. The intramolecular redox process $Ru(0)-NO^+ \rightarrow Ru(II)-NO^-$ results in a five-coordinate, coordinatively unsaturated d^6-ruthenium complex *trans*-[Ru(L1a)(CO)Cl(NO)]. The NMR (^{31}P and ^1H) spectra were consistent with the assigned structures.

Mingos and co-workers also studied complexes of the type *trans*-$[Ru(L1a)Cl(NO)_2](BF_4)$.[87] They assigned this complex a square pyramidal geometry with the L1a ligand occupying *trans*-basal sites. While the structures of $[RuCl(NO)_2(PPh_3)_2]^+$ and $[OsCl(NO)_2(PPh_3)_2]^+$ approximate idealized square pyramidal and trigonal bipyramidal geometries, respectively, the P(1)−Ru−P(2) angle of *trans*-$[Ru(L1a)Cl(NO)_2]^+$ (164.1(1)°) is closer to the angle expected for a square pyramidal complex.[87] In the $[RuCl(NO)_2(PPh_3)_2]^+$ complex, one of the nitrosyl ligands is strongly bent while the other is linear, for the $[OsCl(NO)_2(PPh_3)_2]^+$ complex both nitrosyl ligands are approximately linear, and in the *trans*-$[Ru(L1a)Cl(NO)_2]^+$ complex one nitrosyl ligand is partially bent (156.2(7)°) while the other is approximately linear (172.5(6)°). The ^1H NMR spectroscopy of the *trans*-$[Ru(L1a)Cl(NO)_2](BF_4)$ complex demonstrates inequivalent $-CH_2-$ resonances implying that in either the square pyramidal or trigonal bipyramidal structure the two protons on the methylene group remain in different chemical environments. Thus, any fluxional process that interconverts the square pyramidal and trigonal bipyramidal structures, averaging the methylene environments, does not occur, but the interconversion between the asymmetric and symmetric trigonal bipyramidal intermediates cannot be ruled out.[87]

Finally, Alcock, Brown, and Jeffery determined that the square planar rhodium complex *trans*-$[Rh\{Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2\}(CO)Cl]$ (where $n = 1-3$) reacts reversibly with SO_2 to produce a five-coordinate adduct in which the phosphine ligands were positioned in the axial positions. Only the IR stretches assigned to ν_{c-o} 2030 and ν_{o-s-o} 1220, 1190, and 1060 cm^{-1} were reported to characterize the *trans*-spanning diphosphine complex.[63]

D. Preformed Octahedral Complexes

1. 2,11-Bis(diphenylphosphinomethyl)benzo[c]phenanthrene Derivatives

On the basis of unfavorable steric interactions, L1a forms few six-coordinate molecules.[53] While the reaction of O_2 with *trans*-$[Ir(CO)I(PPh_3)_2]$ occurs readily, the reaction of *trans*-[Ir(L1a)(CO)I] with O_2 requires more forcing conditions (48 h, 130 atm). Moreover, the complete characterization by IR (due to overlapping bands and the presence of residual starting material) or NMR spectroscopy could not be made.[42] Only qualitative reactions were carried out on the addition of halogens, and while immediate reactions were observed in all cases, mixtures of products (some metastable) were also produced.[53] The L1a ligand does not always demonstrate the same properties as the monodentate phosphines (especially in complexes with octahedral geometries); however, the presence of L1a does not prevent the formation of the six-coordinate species.

Oxidative-addition reactions of complexes of the form *trans*-[Ir(L1a)(CO)X] (X = Cl^-, Br^-, and I^-) with hydrogen halides smoothly give six-coordinate species, *trans*-$[Ir(L1a)(CO)X_2H]$,[53] but the analogous *trans*-$[Rh(L1a)(CO)Cl_2H]$ complex did not form on addition of HCl to *trans*-[Rh(L1a)(CO)Cl]. The complexes *trans*-[Ir(L1a)(CO)I] and *trans*-$[Ir(CH_3CN)(L1a)(CO)]^+$ react with H_2, giving *trans*-$[Ir(L1a)(CO)H_2I]$ and *trans*-$[Ir(CH_3CN)(L1a)(CO)H_2]^+$, respectively.[53] It appears that six-coordinate species containing L1a are best obtained if at least one of the ligands is hydrogen.

The preparation of *trans*-$[Ir(L1a)(CO)Cl_3]$ from *trans*-[Ir(L1a)(CO)Cl] and $CuCl_2$ proceeds smoothly at room temperature; however, this is in marked contrast to the action of other oxidants (e.g., PPh_4Cl, Cl_2).[55] The product distribution of the Cl_2 oxidation is strongly dependent on the reaction conditions. These differing product mixtures suggest that multiple kinetic pathways are available, all with similar activation energies.

The X-ray crystal structures of L1a ligand in both the square planar *trans*-[Ir(L1a)(CO)Cl] and the octahedral *trans*-$[Ir(L1a)(CO)Cl_3]$ were compared.[55] For the square planar complex, the P(1)−Ir−P(2) angle is 173.9(2)° and the Cl−Ir−C(CO) angle 168.9(7)°. For the octahedral complex, these angles are 170.7(1)° and 172.6(4)°, respectively.[55] These distortions from the ideal geometries appear to result either from the rigidity of the L1a ligand or from the minimization of its interactions with the other ligands. The largest difference in bond lengths occurs in the Ir−P bond, which increases ca. 0.1 Å on going from the four-coordinate Ir(I) complex to the six-coordinate Ir(III) complex. The longer Ir−P bonds increase the strain imposed on the rigid L1a. This strain may be relieved by decreasing the P(1)−Ir−P(2) angle.

2. Ether Linkages

Metallacrown ethers are a unique class of transition-metal complexes that are formed when α,ω-bis(phosphorus donor)polyether ligands, ligands which contain at least three ether oxygens, are chelated to a transition-metal center. Gray and Duffey reported the first example of a *trans*-coordinated metallacrown ether.[88] This complex was prepared from the photoisomerization of the *cis*-$[Mo\{Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2\text{-}P,P'\}(CO)_4]$ isomer to the *trans*-spanning complex.[88] The single NMR resonances of the chemically equivalent phosphorus atoms and the carbonyl, methylene, and phenyl carbon atoms are potentially sensitive to asymmetry in the phosphine ligands. NMR experiments suggest that the *trans*-spanning metallacrown ether is fluxional and that the $Mo(CO)_4$

group spins freely within the chelate ring to average the environments of the four carbonyl ligands. This rotation appears to slow only when the temperature is lowered to −40 to −80 °C, indicating that the energy barrier to rotation about the P−Mo−P axis is low. While Gray and Duffy suggested that the low rotational barrier was the first direct experimental evidence supporting a lack of significant d−d π-bonding between transition metals and phosphine ligands,[88] this low rotation barrier is not such an indicator because the two d orbitals involved in bonding are degenerate. The X-ray crystal structure of *trans*-[Mo{$Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-*P*,*P*′}$(CO)_4$] demonstrates a P(1)−Mo−P(2) angle of 175.69(4)°, which is consistent with a large, flexible bis(phosphine) ligand.[88] Finally, the four oxygens of the metallacrown ether are essentially planar. The ether ring symmetrically bisects the angle formed from the two carbonyl ligands and the metal center.

While the previously discussed works employed ether linkages in square planar complexes due to their facile synthesis or increased solubility properties, octahedral metallacrown ether linkages are of interest as they may provide pockets or clefts for binding small molecules or ions. The reaction of mercury(II) salts with *cis*-[Mo{$Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$-*P*,*P*′}$(CO)_4$] (MoCE) ($n$ = 4 or 5) is complex, and the product which forms is dependent on the size of the metallacrown ether ring and the anion of the mercury salt.[7,89] The reaction of $HgCl_2$ and the MoCE (n = 5) gives the bimetallic complex *cis*-[Mo{μ-$Ph_2P(CH_2CH_2O)_5CH_2CH_2PPh_2$-*P*,*P*′,*O*,*O*′,*O*″,*O*‴,*O*⁗}$(CO)_4$·$HgCl_2$], because the ether ring is sufficiently large to accommodate Hg^{2+}.[89] The reaction of $Hg(NO_3)_2$·H_2O and MoCE (n = 5) results in the oxidation of the molybdenum complex and the formation of a Hg^{2+} complex of the metallacrown ether ligand. This mercury complex is not formed when $Hg(NO_3)_2$·H_2O is reacted with the free ligand, indicating that the molybdenum complex is required for the reaction to occur.[89] In contrast, the reaction of $HgCl_2$ and MoCE (n = 4) results in the isomerization to *trans*-[Mo{$Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-*P*,*P*′}$(CO)_4$].[89] The Hg^{2+}, which is too large to fit in the n = 4 metallacrown ether, catalyzes the isomerization reaction, perhaps via coordination to the metallacrown ether and a lone pair on one of the carbonyl oxygens.[89]

To determine the range of conformational restraints that could be accommodated by the crown ether backbone, the conformationally restricted α,ω-bis(phosphine)polyether ligand, 1,2-$(Ph_2P(CH_2CH_2O)_2)_2C_6H_4$, was synthesized and then combined with $Mo(CO)_4$(norbornadiene) to yield *cis*-[Mo{1,2-$(Ph_2P(CH_2CH_2O)_2)_2C_6H_4$-*P*,*P*′}$(CO)_4$].[7,90] This complex was isomerized to the *trans*-geometry after treatment with UV light or with $HgCl_2$. The equilibrium constant for the photochemical isomerization of *cis*-[Mo{1,2-$(Ph_2P(CH_2CH_2O)_2)_2C_6H_4$-*P*,*P*′}$(CO)_4$] to *trans*-[Mo{1,2-$(Ph_2P(CH_2CH_2O)_2)_2C_6H_4$-*P*,*P*′}$(CO)_4$] (calculated by integrating ^{31}P NMR spectra) is 0.23, while the equilibrium constant for *cis*-[Mo{$Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-*P*,*P*′}$(CO)_4$] to *trans*-[Mo{$Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-*P*,*P*′}$(CO)_4$] is 1.0 (Figure 18).

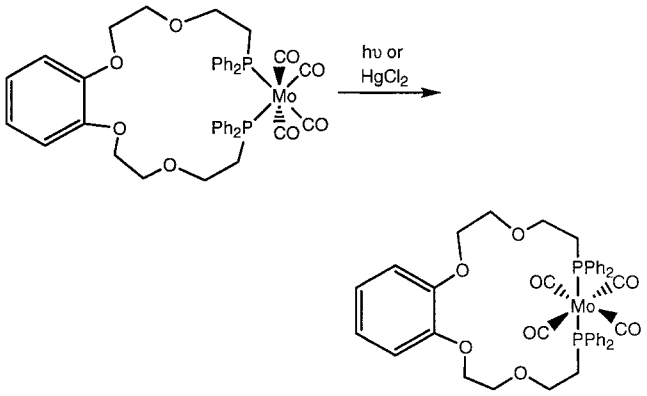


Figure 18. Isomerization of *cis*-[Mo{1,2-$(Ph_2P(CH_2CH_2O)_2)_2C_6H_4$-*P*,*P*′}$(CO)_4$].[7,90]

The relative magnitudes of the equilibrium constants are consistent with the yields of the photochemical reactions (4% for the constrained metallacrown ether versus 45% for the more flexible metallacrown ether). Both observations suggest that the steric contraints imposed by the metallacrown ether favor the *cis*-coordination geometry due to the smaller phosphorus−phosphorus distance.[90]

The reaction of 1,2-$(Ph_2P(CH_2CH_2O)_2)_2C_6H_4$ with *fac*-$[Ru(CO)_3Cl_2(THF)]$ initially yields a mixture of monomeric and oligomeric *cis*,*cis*,*trans*-[Ru{1,2-$(Ph_2P(CH_2CH_2O)_2)_2C_6H_4$-*P*,*P*′}$(CO)_2Cl_2$].[90] The oligomeric ruthenium complexes slowly convert into the monomeric species at ambient temperature in chloroform-*d* solution, suggesting that the oligomeric metallacrown ether complexes are kinetically stable and the monomeric form is thermodynamically stable.[7,90] Notably, the slow interconversion to monomeric species does not occur with the conformationally mobile *cis*,*cis*,*trans*-[Ru{$Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-*P*,*P*′}$(CO)_2Cl_2$] complex and its cyclic dimer.[90] Finally, the ^{13}C NMR chemical shifts of the methylene and phenylene carbons in the metallacrown ethers are affected by both the nature of the metal center and the nature of the ligand. While the carbons of the ether linkage are too far from the metal center to be affected by through-bond interactions, they are quite sensitive to the different steric requirements of the ligands *cis* to the phosphines. This implies that there is a significant interaction between the spanning ether linkage and the ligands on the metal center.

The reaction of $Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$ (n = 4 or 5) with $Ru(CO)_3Cl_2(THF)$ gives a variety of complexes, the major one being *cis*,*cis*,*trans*-[Ru{$Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$-P,P′}$(CO)_2Cl_2$].[7,91] While *trans*-spanned square planar complexes generally have coordination chemical shifts which increase as the length of the linkage decreases, the opposite trend is observed in the ^{31}P NMR spectroscopy of the *trans*-spanning monomers with metallacrown ethers. Also, the single ^{13}C NMR resonance that is observed indicates that the $Ru(CO)_2Cl_2$ group moves freely within the chelate ring to average the environments of the two carbonyl ligands. A comparison of *cis*,*cis*,*trans*-[Ru{$Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$-P,P′}$(CO)_2Cl_2$] and *trans*-[Mo{$Ph_2P(CH_2CH_2O)_4CH_2CH_2PPh_2$-*P*,*P*′}$(CO)_4$] suggests the barrier to rotation

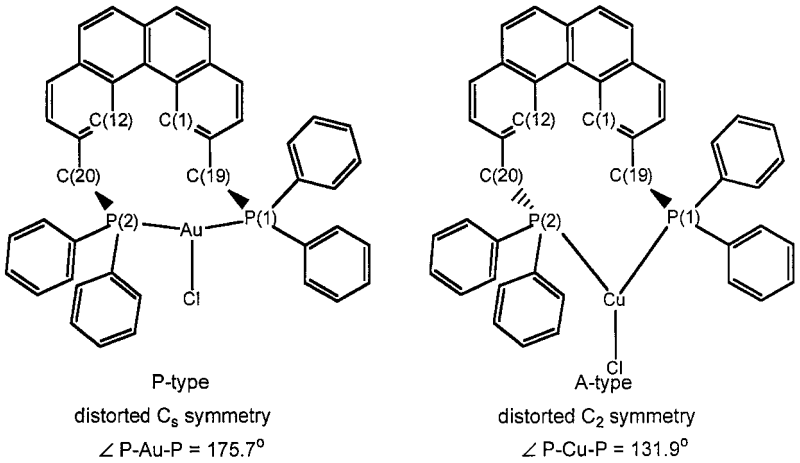


Figure 19. Examples of P-type (parallel-type) and A-type (antiparallel-type) coordination of the L1a ligand. Complexes with P−M−P angles > 155° prefer P-type coordination, while complexes with P−M−P angles < 140° prefer A-type coordination. Complexes with P−M−P angles between 140° and 155° may have either P- or A-type coordination.[93]

about the P−M−P axis is lower in the ruthenium complex than in the molybdenum complex.[91] The lower rotation barrier could be due to the fact that the carbonyl ligands in the ruthenium complex can be averaged by rotating the $Ru(CO)_2Cl_2$ moiety so that the *trans*-spanning ligand moves over the smaller chlorides but not over the larger carbonyl ligands.

Two different rotamers of *cis,cis,trans*-[$Ru(CO)_2Cl_2${$Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$-*P,P′*}] are observed in the solid state. The major rotamer (70%) has the *trans*-spanning ligand passing between one chloride and one carbonyl, while in the minor rotamer (30%) the *trans*-spanning ligand passes between the two chlorides. The presence of rotamers in the crystal structure may be due to the fact that rotation about the P−Ru−P bond does not affect the orientation of the phenyl rings or the *trans*-spanning polyether chain. Gray and co-workers propose that the third possible rotamer (that with the *trans*-spanning linkage passing between the two carbonyls) is not observed because a less stable conformation prevents cocrystallization with the other two rotamers. This hypothesis is supported by the fact that the conformation of the *trans*-spanning ligand in the ruthenium complex is very different from that in the molybdenum complex, as indicated by the torsion angles that differ by as much as 60°.[91] The minor synthesis products include a dimer, *cis,cis,trans*-[Ru{$Ph_2P(CH_2CH_2O)_nCH_2CH_2PPh_2$-*P,P′*}$(CO)_2Cl_2]_2$, the first example of a dimetallacrown ether.[91]

3. Phosphinocalix[4]arene and Phosphinocyclodextrin Linkages

Matt and co-workers also synthesized octahedral complexes using preformed, *trans*-spanning {$(Ph_2P)_2$-substituted calix[4]arene} ligands. Reaction of ruthenium trichloride with carbon monoxide followed by the addition of the substituted calix[4]arene ligand yielded the complex *cis,cis,trans*-[$Ru(CO)_2Cl_2${$(Ph_2P)_2$-substituted calix[4]arene}].[29] Here, the *cis*-arrangement of the two carbonyl ligands was inferred from the infrared spectrum, which showed two $\nu_{C\equiv O}$ bands at 2072 and 1995 cm^{-1}. This complex was further observed to isomerize in 1,2-dichloroethane into the *trans,trans,trans*-[$Ru(CO)_2Cl_2${$(Ph_2P)_2$-substituted calix[4]arene}] isomer.[29] The *trans*-spanning behavior was confirmed by X-ray crystallography, where it was demonstrated that the P(1)−Ru−P(2) bond angle was 172.2(3)°. Notably, the distance between the phenyl rings of the phosphine ligand and the intercalated CO ligand is small (ca. 2.75 Å), suggesting a bonding interaction between the sandwiched CO and the phenyl substitutents on the phosphine. The relatively low-frequency infrared absorption band ($\nu_{C\equiv O}$ 1924 cm^{-1}) supports this assumption.[29]

Shimizu and co-workers studied the catalytic activity of [Rh(acac)$(CO)_2$] in the presence of (*m*-$MOSO_2C_6H_4)_2P)_2$-substituted calix[4]arenes (where M = 9 Na^+ and 1 H^+ or 10 Na^+).[92] These materials were synthesized due to their attractive water solubilities as well as their promising inverse phase-transfer catalytic properties when used in homogeneous, aqueous hydroformylation reactions. It should be noted that the Rh catalysts were not well characterized structurally, so the *trans*-spanning nature of the calix[4]arene ligands remains questionable.

E. Additional Comments

The following studies regarding the L1a ligand and its derivatives transcend metal geometries and thus have been grouped here as respresentative of the influence of the ligand on metal coordination. The crystal structures of the uncoordinated (free) bidentate phosphine ligands, L1a, L1b, and L1c,[20,21] were compared with the crystal structures of their transition-metal complexes,[93] and it was determined that these ligands can coordinate to the metal centers in one of two conformations. In the first conformation, designated P-type (for parallel), the C(19)−P(1) and C(20)−P(2) vectors are pointing toward the same side of the mean benzo[*c*]phenanthrene plane (Figure 19). In the second conformation, designated A-type (for antiparallel), the same vectors point to opposite sides of the benzo[*c*]phenanthrene plane.

Significant deviations from planarity occur in both the uncoordinated ligands and coordination complexes due to interaction between the hydrogen atoms on C(1) and C(12).[93] The effect of the H(1)−H(12) overlap was determined from the tilt angle "*β*", which

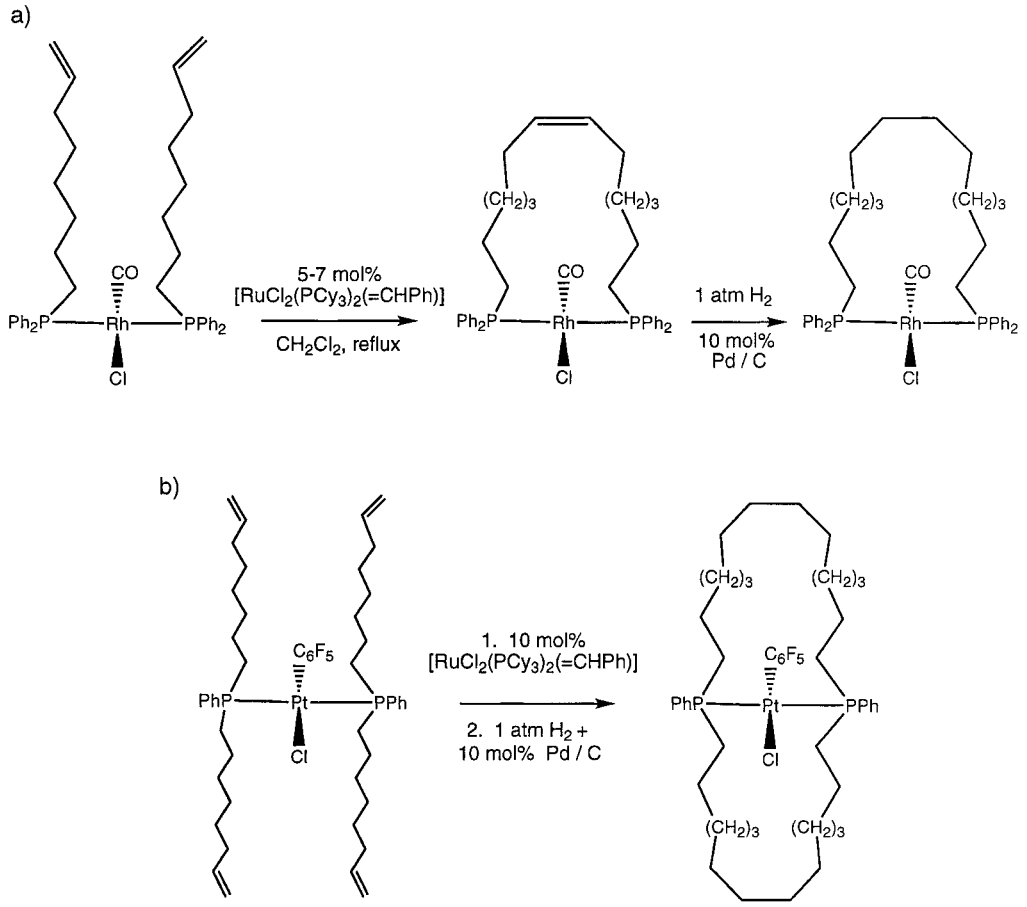


Figure 20. (a) In situ preparation of *trans*-[Rh{$Ph_2P(CH_2)_{14}PPh_2$}Cl(CO)].[80] (b) The first example of a dimacrocyclization reaction to produce two *trans*-spanning diphosphine linkages, *trans*-[Pt{$PhP((CH_2)_{14})_2PPh$}Cl(C_6F_5)].[94]

is defined as the dihedral angle between the two terminal aromatic ring planes of the benzo[*c*]phenanthrene moiety.[93] For ligand L1a, the tilt angle β was 21.6°; for L1b, it was 26.9°; the difference between these two angles was attributed to packing forces. Complex formation between L1a or L1b and Cu, Ag, Au, Hg, Pd, Rh, Ir, or Ru induced large changes in angle β. For all P-type complexes, the β values fall in the range 17−27°, while for the A-type complexes, the β-values range from 28 to 36° (all except one being >32°).[93] Additionally, larger P(1)−M−P(2) angles (α-angles) are associated with P-type conformations (142−176°) and smaller P(1)−M−P(2) angles with A-type conformations (126−162°). Both conformations were found to exist in the middle of the range (142−162°).[93]

Finally, analysis of the conformational angles indicates an intrinsic difference in conformational flexibility between the A- and P-type structures.[93] A-type conformations are considered slightly distorted C_2-symmetrical structures; thus, they are more conformationally flexible than the P-type conformations which may be considered distorted C_s-symmetric structures. For α angles >160°, strain in the hydrocarbon backbone prevents adoption of the A-type conformation; therefore, P-type conformation is observed. For α angles <140°, the A-type conformation is clearly preferred. Again, in the middle of the range, it cannot be determined which conformation will be preferred.[93]

III. In Situ Ligand Strategy

A. In Situ Square Planar Complexes

An in situ *trans*-spanning preparation for square planar complexes has very recently been reported by Gladysz and co-workers.[94] In this work, [Rh(μ-Cl)(COD)]$_2$, carbon monoxide, and $PPh_2(CH_2)_6CH{=}CH_2$ yielded the *trans*-[Rh{$PPh_2(CH_2)_6CH{=}CH_2$}$_2$}(CO)Cl] complex. This *trans*-configured complex was reacted over Grubbs' catalyst ($RuCl_2(PCy_3)_2(=CHPh)$)[95] and then hydrogenated over Pd/C to yield the saturated, *trans*-spanning complex *trans*-[Rh{$PPh_2(CH_2)_{14}PPh_2$}(CO)Cl] (Figure 20a). Similar procedures were used to produce *trans*-[Pt{$PPh_2(CH_2)_{14}PPh_2$}Cl(C_6F_5)]. Notably, the complications due to cyclometalation which are often observed with preformed, *trans*-spanning diphosphine containing saturated hydrocarbon linkages (vide infra) were avoided in this catalyzed in situ method. Additionally, Gladysz and co-workers also provided the first demonstration of doubly *trans*-spanning diphosphine complexes (Figure 20b) as this method can be used in dimacrocyclization and trimacrocyclization reactions.[94]

B. In Situ Octahedral Complexes

In contrast to square planar complexes, relatively few *trans*-spanning octahedral complexes have been reported in the literature. This difference arises because the group bridging the two phosphines must

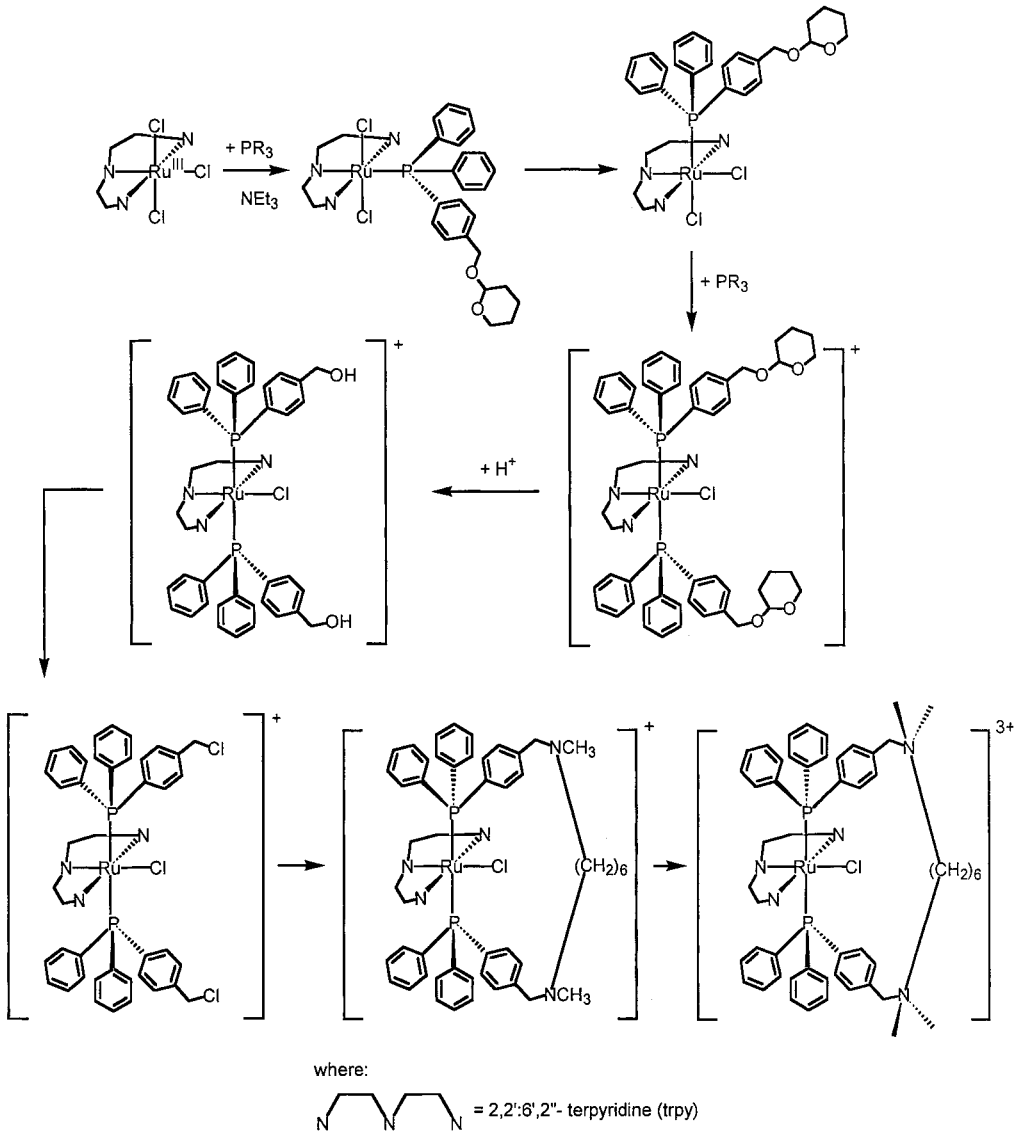


Figure 21. Generalized synthesis for the preparation of *trans*-[Ru{Ph_2P-benzyl−$N(Me)_2$−$(CH_2)_6$−$N(Me)_2$−benzyl−PPh_2}-$Cl(trpy)]^{3+}$.[96]

be much longer in octahedral complexes than in square planar complexes if the span is to wrap around the *cis*-coordinated ligands.[88] These longer bridging groups are more likely to coordinate to a second metal and form unwanted polymers. A second method for the synthesis of complexes containing a *trans*-spanning bidentate phosphine ligand, the in situ ligand strategy, was developed to combat this obstacle.

The in situ ligand strategy for the generation of complexes containing *trans*-spanning diphosphine ligands was first developed and utilized by Takeuchi et al.[96,97] Using the in situ ligand strategy, Takeuchi and co-workers synthesized *trans*-spanning octahedral complexes of the form *trans*-$[Ru(L2)Cl(trpy)]^+$, where L2 = $Ph_2PC_6H_4CH_2N(Me)(CH_2)_nN(Me)CH_2C_6H_4Ph_2$ or $(Ph_2PC_6H_4CH_2N(Me_2)(CH_2)_nN(Me)_2CH_2C_6H_4PPh_2)^{2+}$ (n = 5 or 6), by linking two-coordinated *trans*-positioned tertiary phosphine ligands with a diamine (Figure 21).[96] These complexes are the first reported cases of in situ generated, *trans*-spanning ligands on an octahedral metal center. Like the preformed ligand strategy which employs alkyl, ether, or acetylenic *trans*-spanning linkages, the in situ ligand strategy offers flexibility in terms of both backbone length and composition while an additional benefit of the in situ ligand strategy results from the absence of cyclometalated products.[96]

UV−vis spectroscopy for the *trans*-$[Ru(L2)Cl(trpy)]^+$ complexes shows no change in the wavelength maximum relative to the unspanned benzyl chloride or the monoalkylated or dialkylated amine *trans*-spanned complexes. This observation indicates that the cyclization of the span on the periphery of the ligand structure leaves the electronic environment surrounding the metal center unchanged. The electrochemical data also show that once the phosphine ligands are coordinated to the metal center, no appreciable change in the redox potential of the ruthenium(III)/(II) couple is observed. However, the shapes of the cyclic voltammograms do show a dependence on the identity of the *trans*-spanning linkage. The irreversible behavior of the complexes containing tertiary amine linkages is attributed to the oxidation of the tertiary amine after the oxidation of the ruthenium(II) center. Quaternary amine link-

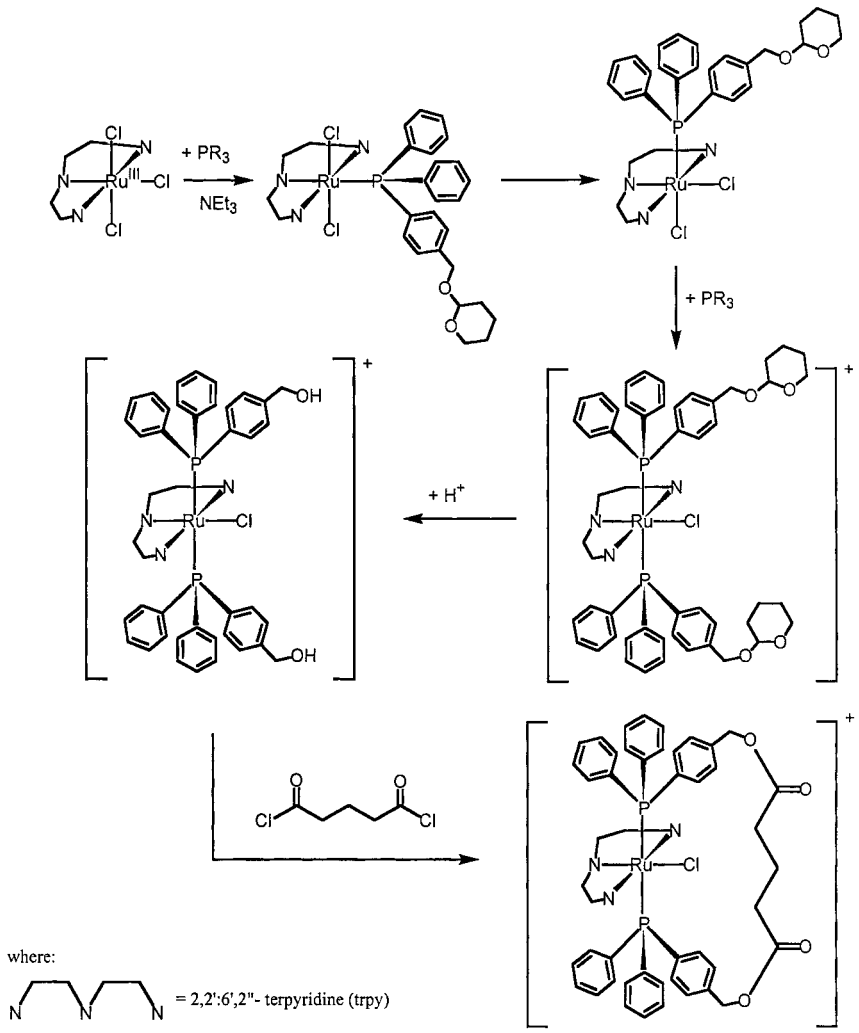


Figure 22. Reaction scheme for the preparation of *trans*-[Ru(C3SPAN)Cl(trpy)]$^+$.[97]

ages make the *trans*-spanning linkage less susceptible to oxidation; however, dealkylation occurred with change in pH.[96]

To overcome the disadvantages associated with ligand oxidation and dealkylation, a second series of complexes with an ester linkage was synthesized, *trans*-[Ru(L3)Cl(trpy)]$^+$, where L3 = $Ph_2PC_6H_4$-$CH_2O(CO)Y(CO)OC_6H_5PPh_2$ and Y = $(CH_2)_3$ = C3SPAN, $(CH_2)_4$ = C4SPAN, isophthalate = ISPAN using the in situ spanning strategy (Figure 22).[97] Again, use of the in situ strategy retains the span versatility in term of both length and structure, while the ester linkage provides a span that is stable to degradation by oxidation, reduction, and hydrolysis (pH = 2−10). The crystal structure analysis of *trans*-[Ru(C4SPAN)(Cl)(trpy)]$^+$ demonstrates a P(1)−Ru−P(2) bond angle of 178.1(1)°, indicating little strain in the *trans*-spanning conformation. Notably, the spanning linkage is positioned in one of the two pockets defined by the chloride ligand and the terminal pyridine groups of trpy.

Variable temperature ^{1}H and ^{13}C NMR spectra of the *trans*-[Ru(L3)(Cl)(trpy)]$^+$ complexes are consistent with a flexible spanning linkage that does not demonstrate restricted rotation about either the P−C_{ipso} or the Ru−P bonds even at low temperatures (−78 °C).[97] Two types of motion appear to be available in the *trans*-spanning complexes. The first involves a complete 360° rotation of the span about the P−Ru−P axis, where the span passes over both the chloride and meridional trpy ligand. The second involves a restricted "fan-like" motion of the spanning linkage limited by the two terminal pyridines of the trpy ligand, where the span passes over only the chloride ligand and the not the trpy ligand. Both mechanisms would time average the trpy resonances, and thus, it is not possible, at this time, to distinguish which motional mechanism operates.

IV. Heterogeneous Complexes

While we have elected not to include a comprehensive review of heterogeneous *trans*-spanning diphosphine complexes, we do include a few examples of the synthesis and reactivity of the polymer-bound complexes as representative examples.

Bailar and co-workers prepared selective heterogeneous catalysts from the reaction of polymeric diphenylbenzylphosphine and either Pd(II)Cl_2 or Pt(II)Cl_2.[98] These catalysts were assigned exclusively to *trans*-diphosphine configurations based on their IR spectra which show M−Cl stretches at 351 and 339 cm^{-1} for Pd and Pt, respectively.[98] The palladium- and platinum-containing polymeric hydro-

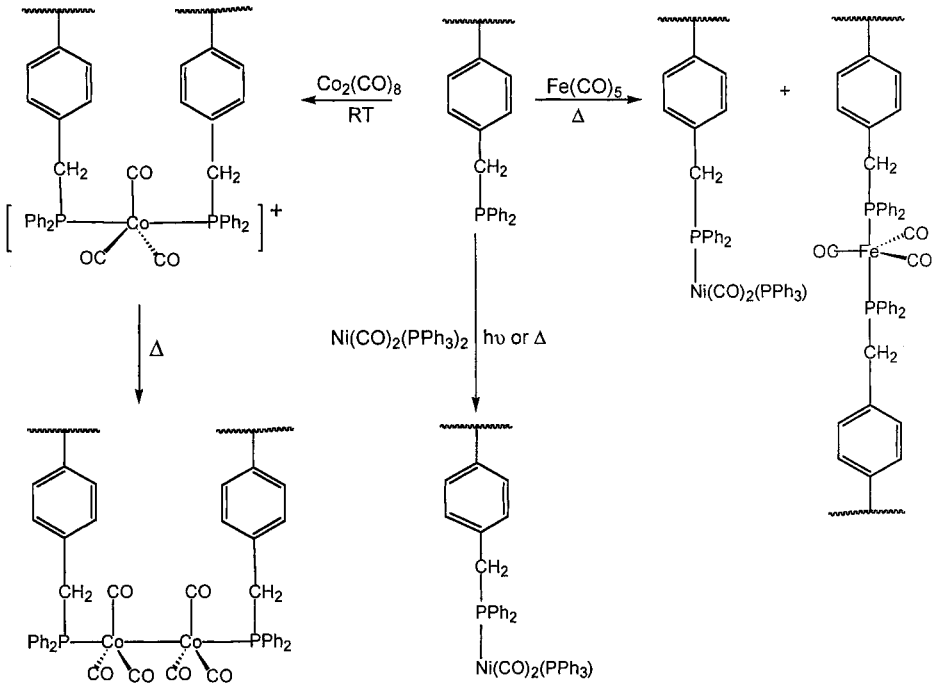


Figure 23. Typical reactions which occurred between metal carbonyls and polymeric ligands.[99]

genation catalysts display good selectivity for the reduction of polyolefins and monoolefins. In alcohol solvents, the Pd-containing polymer hydrogenates olefins at room temperature under hydrogen gas (1 atm) within 3−6 h. Other solvents require higher pressures (ca. 37 atm) for the same reaction rate. The catalytic activity of the metal-containing polymers decreases as the quantity of the metal in the polymer decreases. The platinum-containing polymer requires more forcing conditions than the palladium polymer, i.e., the addition of $SnCl_2$ and reactions conditions of 150 °C and 550 psi hydrogen.[98] Finally, both the Pd and Pt polymer catalysts could be recycled several times with only a small loss in catalytic activity after the first use and no further loss thereafter.[98] The hydrogenation of several hexadiene isomers (2,4-hexadiene, 1,3-hexadiene, and 1,5-hexadiene) proceeded with the conjugated isomers being reduced more rapidly and with greater selectivity than the nonconjugated isomers. The (polymer−phosphine)-palladium catalyst was activated by alcohol solvents. Deuteration studies showed exchange reactions occur much more readily than either the isomerization or reduction of the olefins. It was determined that the atmosphere was the primary source of hydrogen for the reductions in alcohol and other solvents. The generation of gaseous products of the exchange reaction between the alcohol proton and the atmosphere is believed to occur after the hydrogenation reaction.[98]

The linear and cross-linked polymeric analogues of benzyldiphenylphosphine were synthesized by the reaction of lithium diphenylphosphide ($LiPPh_2$) with the corresponding chloromethylated polystyrene and styrene/divinylbenzene resin, respectively. The polymeric analogue of triphenylphosphine was prepared by reaction of $LiPPh_2$ and brominated styrene/divinylbenzene resin, but it contained a significant amount of residual bromide.[99] Pittman and co-workers then prepared polymeric analogues of a variety of metal carbonyls, using both thermal and photochemical techniques to incorporate Fe, Rh, Co, Cr, Mo, W, Mn, and Ni metal complexes.[99] The CO stretching frequencies indicate that resin-bound derivatives of the Cr, Mo, and W hexacarbonyls and iron pentacarbonyl have a *trans*-diphosphine configuration (Figure 23).

The use of the polymeric (linear and cross-linked) derivatives of dicobalt hexacarbonyl result in a catalyst that is readily recycled and gives product yields for the hydroformylation of 1- and 2-pentenes that are quite similar to those of the homogeneous species.[99] The cyclization of ethyl propiolate was performed with polymer−nickel catalysts. Finally, benzene isomers were isolated with the initial use of a polymer−nickel catalyst, whereas benzene and cyclooctatetrene isomers were observed using the recycled catalyst.[99] The catalytic reactivity of the *trans*-diphosphine complexes was not reported.

V. Conclusions

Historically, the use of bidentate ligands in coordination chemistry was first developed with *cis*-chelation in mind. While a rich chemistry has developed involving bidentate *cis*-chelating ligands, the preparation of bidentate *trans*-spanning tertiary phosphine ligands has remained a synthetic challenge. Two types of synthetic routes have emerged, namely, the preformed ligand strategy and the in situ ligand strategy. The preformed ligand strategy has met with much success, resulting in the production of a variety of transition-metal complexes containing a number of *trans*-spanning bidentate tertiary phosphine ligands. Notably, both flexible and rigid *trans*-spanning bidentate tertiary phosphine ligands have been successfully employed, which proved contrary to basic intuition regarding the formation of large flexible rings. The in situ ligand strategy is a much

less frequently used strategy, but it has real potential, especially when synthetic routes for the introduction of *trans*-positioned monodentate tertiary phosphine ligands have already been developed for a specific metal center of interest.

Development of the chemistry and reactivity of transition-metal complexes that contain *trans*-spanning bidentate tertiary phosphine ligands remains a challenge. The favorable structural properties of *trans*-spanning tertiary phosphine ligands are clear: unusual metal geometries can be enforced, certain ligand positions can be sterically crowded or sheltered, and the *trans*-spanning linkages can be modified to include a variety of structures. Furthermore, there are already examples of interesting reactivity of transition-metal complexes that contain two monodendate tertiary phosphine ligands.[100] However, to fully realize the reactive potential of transition-metal complexes that contain *trans*-spanning tertiary phosphine ligands, it may be necessary to develop *trans*-spanning ligands that are held tightly in position so that isomerization or loss of the *trans*-spanning ligand is reduced or eliminated during any reaction or catalytic process.

VI. Abbreviations

Me	methyl
Et	ethyl
Pr	propyl
t-Bu	*tert*-butyl
Ph	phenyl
Cy	cyclohexyl
COD	cycloocta-1,5-diene
trpy	2,2′:6′,2″-terpyridine
acac	acetylacetonate
dmad	dimethylacetylenedicarboxylate
tcne	tetracyanoethylene
THF	tetrahydrofuran
dpe	$Ph_2P(CH_2)_2PPh_2$
dph	$Ph_2P(CH_2)_6PPh_2$
dphp	$Ph_2P(CH_2)_7PPh_2$
dpo	$Ph_2P(CH_2)_8PPh_2$
dpn	$Ph_2P(CH_2)_9PPh_2$
dpd	$Ph_2P(CH_2)_{10}PPh_2$
dpu	$Ph_2P(CH_2)_{11}PPh_2$
dpdod	$Ph_2P(CH_2)_{12}PPh_2$
dphd	$Ph_2P(CH_2)_{16}PPh_2$
dpdo	1,8-bis(diphenylphosphino)-3,6-dioxaoctane
bdpbz	$Ph_2P(o\text{-}C_6H_4)CH_2CH_2(o\text{-}C_6H_4)PPh_2$
bdabz	$Ph_2As(o\text{-}C_6H_4)CH_2CH_2(o\text{-}C_6H_4)AsPh_2$
bdph	1,6-bis(diphenylphosphino)-*trans*-hex-3-ene
bdpps	2,2′-bis(*o*-diphenylphosphino)-*trans*-stilbene
bdtps	2,2′-bis(di-*o*-tolylphosphino-*trans*-stilbene)
4-PADA	4-pyridine-4-azo-4′-(*N*,*N*′-dimethyl)aniline
PSP	$(C_6H_5)_2P(CH_2)_2S(CH_2)_2P(C_6H_5)_2$
pop	3,3′-oxybis[(diphenylphosphino)methylbenzene]
POP	bis(2-diphenylphosphinoethyl)oxide, $(C_6H_5)_2P(CH_2)_2O(CH_2)_2P(C_6H_5)_2$
pop-2H	[3,3′-oxybis[((diphenylphosphino)methyl)-benzene]ato-$C^2,C^{2'}$-$P-P'$]$^{2-}$
(m-CF_3)$_4$pop	bis{3-bis(3-trifluoromethylphenyl)phosphinomethyl]phenyl}ether
PC_4P	1,4-bis(diphenylphosphino)butane, $(C_6H_5)_2P(CH_2)_4P(C_6H_5)_2$
poop	[ethylenebis(oxyethylene)]bis(diphenylphosphine)
PC_5P	1,5-bis(diphenylphosphino)pentane $(C_6H_5)_2P(CH_2)_5P(C_6H_5)_2$
L1a	2,11-bis(diphenylphosphinomethyl)benzo[*c*]-phenanthrene

VII. Acknowledgments

This work was supported, in part, from grants from the Research Corporation (ROA Program for K.J.T. and CC4252 for C.A.B.). C.A.B. acknowledges the award of a Bunting Fellowship given by the Radcliffe Institute of Advanced Studies at Harvard University, and P.A. also acknowledges financial support from the Howard Hughes Medical Institute Program at Villanova University.

VIII. References

(1) For a collection of some of the papers by Alfred Werner, see: Kauffman, G. B. In *Classics in Coordination Chemistry, Part 1: The Selected Papers of Alfred Werner*; Dover Publications: New York, 1968.
(2) Werner, A. *Ber. Deut. Chem. Gesell.* **1911**, *44*, 1887.
(3) Drew, H. D. K.; Tress, H. *J. Chem. Soc.* **1933**, 1335.
(4) Issleib, V. K.; Hohlfeld, G. *Z. Anorg. Allg. Chem.* **1961**, *312*, 169.
(5) O'Brien, T. In *Chemistry of the Coordination Compounds*; Bailar, J. C., Jr., Ed.; Chapman and Hall Ltd.: New York, 1956; pp 253−260.
(6) Ogino, H. *J. Coord. Chem.* **1987**, *15*, 187.
(7) Gray, G. M. *Comm. Inorg. Chem.* **1995**, *17* (2), 95.
(8) Minahan, D. M. A.; Hill, W. E.; McAuliffe, C. A. *Coord. Chem. Rev.* **1984**, *55*, 31.
(9) Shaw, B. L. *J. Organomet. Chem.* **1980**, *200*, 307.
(10) Sandee, A. J.; van der Veen, L. A.; Reek, J. N. H.; Kamer, R. C. J.; Lutz, M.; Spek, A. L.; van Leeuwen, P. W. N. M. *Angew. Chem., Int. Ed.* **1999**, *38* (21), 3231.
(11) Sato, M.; Shigeta, H.; Sekino, M.; Akabori, S. *J. Organomet. Chem.* **1993**, *458*, 199.
(12) van der Veen, L. A.; Keeven, P. H.; Schoemaker, G. C.; Reek, J. N. H.; Kamer, P. C. J.; van Leeuwen, P. W. N. M., Lutz, M.; Spek, A. L. *Organometallics* **2000**, *19*, 872.
(13) Kranenburg, M.; van der Burgt, Y. E. M.; Jamer, P. C. J.; Goubitz, K.; Fraanje, J. *Organometallics* **1995**, *14*, 3081.
(14) Gorla, F.; Venanzi, L. M.; Albinati, A. *Organometallics* **1994**, *13*, 43.
(15) Haenel, M. W.; Jakubik, D.; Kruger, C.; Betz, P. *Chem. Ber.* **1991**, *124*, 333 and references therein.
(16) Haenel M. W.; Jakubik, D.; Rothenberger, E.; Schroth, G. *Chem. Ber.* **1991**, *124*, 1705.
(17) Timmer, K.; Thewissen, D. H. M. W.; Marsman, J. W. *Recl. Trav. Chim. Pays-Bas* **1988**, *107*, 248.
(18) DeStefano, N. J.; Johnson, D. K.; Lane, R. M.; Venanzi, L. M. *Helv. Chim. Acta* **1976**, *59* (8), 2674.
(19) Kapoor, P. N.; Venanzi, L. M. *Helv. Chim. Acta* **1977**, *60* (277), 2824.
(20) Hirschfeld, F. L.; Sandler, S.; Schmidt, G. M. *J. Chem. Soc.* **1963**, 2108.
(21) Hirschfeld, F. L. *J. Chem. Soc.* **1963**, 2126.
(22) Barrow, M.; Burgi, H. B.; Johnson, D. K.; Venanzi, L. M. *J. Am. Chem. Soc.* **1976**, *98*, 2356.
(23) Johnson, D. K.; Pregosin, P. S.; Venanzi, L. M. *Helv. Chim. Acta* **1976**, *59* (8), 2691.
(24) Barrow, M.; Burgi, H. B.; Camalli, M.; Caruso, F.; Fischer, E.; Venanzi, L. M.; Zambonelli, L. *Inorg. Chem.* **1983**, *22*, 2356.
(25) (a) Camalli, M.; Caruso, F.; Chaloupka, S.; Kapoor, P. N.; Pregosin, P. S.; Venanzi, L. M. *Helv. Chim. Acta* **1984**, *67*, 1603. (b) Camalli, M.; Caruso, F.; Chaloupka, S.; Venanzi, L. M. *Helv. Chim. Acta* **1988**, *71*, 703.
(26) Boron-Rettore, P.; Grove, D. M.; Venanzi, L. M. *Helv. Chim. Acta* **1984**, *67* (1), 65.
(27) Marty, W.; Kapoor, P. N.; Buergi, H.-B.; Fischer, E. *Helv. Chim. Acta* **1987**, *70*, 158.
(28) Wieser, C.; Matt, D.; Fischer, J.; Harriman, A. *J. Chem. Soc., Dalton Trans.* **1997**, 2391.
(29) Wieser-Jeunesse, C.; Matt, D.; De Cian, A. *Angew. Chem., Int. Ed. Engl.* **1998**, *37* (20), 2861.
(30) Armspach, D.; Matt, D. *Chem. Commun.* **1999**, 1073.
(31) Pryde, A. J.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Chem. Commun.* **1973**, 947.
(32) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd ed.; Wiley: New York, 1972; p 652.

(33) Pryde, A.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1976**, 322.
(34) Shaw, B. L. *J. Am. Chem. Soc.* **1995**, *97*, 3856.
(35) (a) Beesley, P. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc.* **1915**, *107*, 1080. (b) Ingold, C. K. *J. Chem. Soc.* **1921**, *119*, 305. (c) Ingold, C. K. *J. Chem. Soc.* **1921**, *119*, 951.
(36) Al-Salem, N. A.; Empsall, H. D.; Markham, R.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1979**, 1972.
(37) March, F. C.; Mason, R.; Thomas, K. M.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1975**, 584.
(38) Crocker, C.; Errington, R. J.; Markham, R.; Moulton, C. J.; Odell, K. J.; Shaw, B. L. *J. Am. Chem. Soc.* **1980**, *102*, 4373.
(39) Crocker, C.; Empsall, H. D.; Errington, R. J.; Hyde, E. M.; McDonald, W. S.; Markham, R.; Norton, M. C.; Shaw, B. L.; Weeks, B. *J. Chem. Soc., Dalton Trans.* **1982**, 1217.
(40) Al-Salem, N. A.; McDonald, W. S.; Markham, R.; Norton, M. C. Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1980**, 59.
(41) Hill, W. E.; Minahan, D. M. A.; Taylor, J. G.; McAuliffe, C. A. *J. Am. Chem. Soc.* **1982**, *104*, 6001.
(42) Parish, R. V.; Razzoki, S. M. *Inorg. Chim. Acta* **1985**, *96*, 49.
(43) Hill, W. E.; McAuliffe, C. A.; Niven, I. E.; Parish, R. V. *Inorg. Chim. Acta* **1980**, *38*, 273.
(44) Clark, P. W. *J. Organomet. Chem.* **1976**, *110*, C13.
(45) Bennett, M. A.; Johnson, R. N.; Tomkins, I. B. *J. Organomet. Chem.* **1977**, *128*, 73.
(46) Bennett, M. A.; Clark, P. W. *J. Organomet. Chem.* **1976**, *110*, 367.
(47) (a) Cheney, A. J.; Mann, B. E.; Shaw, B. L.; Slade, R. M. *J. Chem. Soc., Dalton Trans.* **1971**, 3833. (b) Cheney, A. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1972**, 255. (c) Cheney, A. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1973**, 860.
(48) Briggs, J. C.; McAuliffe, C. A.; Hill, W. E.; Minahan, D. M. A.; Taylor, J. G.; Dyer, G. *Inorg. Chem.* **1982**, *21*, 4204.
(49) DeStefano, N. J.; Johnson, D. K.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1974**, *13* (2), 133.
(50) DeStefano, N. J.; Johnson, D. K.; Venanzi, L. M. *Helv. Chim. Acta* **1976**, *59* (8), 2683.
(51) Balch, A. L.; Neve, F.; Olmstead, M. M. *Inorg. Chem.* **1991**, *30*, 3395.
(52) Nixon, J. F.; Pidcock, A. *Annu. Rev. NMR Spectrosc.* **1969**, *2*, 345.
(53) Reed, F. J. S.; Venanzi, L. M. *Helv. Chim. Acta* **1977**, *60* (8), 2804.
(54) Bachechi, F.; Zambonelli, L.; Venanzi, L. M. *Helv. Chim. Acta* **1977**, *60* (8), 2815.
(55) Baumgartner, E. R.; Reed, F. J. S.; Venanzi, L. M.; Bachechi, F.; Mura, P.; Zambonelli, L. *Helv. Chim. Acta* **1983**, *66* (8), 2572.
(56) Bracher, G.; Grove, D. M.; Venanzi, L. M.; Bachechi, F.; Mura, P.; Zambonelli, L. *Helv. Chim. Acta* **1980**, *63* (8), 2519.
(57) Kapoor, P. N.; Pregosin, P. S.; Venanzi, L. M. *Helv. Chim. Acta* **1982**, *65* (3), 654.
(58) Elding, L. I.; Kellenberger, B.; Venanzi, L. M. *Helv. Chim. Acta* **1983**, *66* (6), 1676.
(59) Bracher, G.; Kellenberger, B.; Venanzi, L. M.; Bachechi, F.; Zambonelli, L. *Helv. Chim. Acta* **1988**, *71*, 1442.
(60) Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933.
(61) Baltensperger, U.; Gunter, J. R.; Kagi, S.; Kahr, G.; Marty, W. *Organometallics* **1983**, *2* (5), 571.
(62) Kapoor, P. N. *J. Organomet. Chem.* **1988**, *341*, 363.
(63) Alcock, N. W.; Brown, J. M.; Jeffrey, J. C. *J. Chem. Soc., Chem. Commun.* **1974**, 829.
(64) Alcock, N. W.; Brown, J. M.; Jeffery, J. C. *J. Chem. Soc., Dalton Trans.* **1976**, 583.
(65) Timmer, K.; Thewissen, D. H. M. W. *Inorg. Chim. Acta* **1985**, *100*, 235.
(66) Alcock, N. W.; Brown, J. M.; Jeffery, J. C. *J. Chem. Soc., Dalton Trans.* **1977**, 888.
(67) Mochida, I.; Mattern, J. A.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 3021.
(68) Hill, W. E.; Taylor, J. G.; McAuliffe, C. A.; Muir, K. W.; Manojlovic-Muir, L. *J. Chem. Soc., Dalton. Trans.* **1982**, 833.
(69) Sacconi, L.; Dapporto, P. *J. Am. Chem. Soc.* **1970**, *92*, 4113.
(70) Dapporto, P.; Sacconi, L. *J. Chem. Soc. (A)* **1971**, 1914.
(71) Hill, W. E.; Taylor, J. G.; McAuliffe, C. A.; Levason, W. *J. Chem. Soc., Dalton. Trans.* **1982**, 841.
(72) Hill, W. E.; Taylor, J. G.; Falshow, C. P.; King, T. J.; Beagley, B.; Tonge, D. M.; Pritchard, R. G.; McAuliffe, C. A. *J. Chem. Soc., Dalton Trans.* **1986**, 2289.
(73) Smith, D. C., Jr.; Gray, G. M. *Inorg. Chem.* **1998**, *37*, 1791.
(74) Smith D. C.; Gray G. M. *J. Chem. Soc., Dalton Trans.* **2000**, *5*, 677.
(75) Schwarzenbach, G. *Helv. Chim. Acta* **1966**, *49*, 1927.
(76) Sacconi, L.; Gelsomini, J. *Inorg. Chem.* **1968**, *7*, 291.
(77) Mason, R.; Scollary, G. R. *Aust. J. Chem.* **1978**, *31*, 781.
(78) Mason, R.; Scollary, G. R.; Moyle, B.; Hardcastle, K. I.; Shaw, B. L.; Moulton, C. J. *J. Organomet. Chem.* **1976**, *113*, C49.
(79) Empsall, H. D.; Mentzer, E.; Pawson, D.; Shaw, B. L.; Mason, R.; Williams, G. A. *J. Chem. Soc., Chem. Commun.* **1977**, 311.
(80) van den Beuken, E. K.; Meetsma, A.; Kooijman, H.; Spek, A. L.; Feringa, B. L. *Inorg. Chim. Acta* **1997**, *264*, 171.
(81) Boyce, B. A.; Carroy, A.; Lehn, J.-M.; Parker, D. *J. Chem. Soc., Chem. Commun.* **1984**, 1546.
(82) It should be noted that mass spectrometry is often not reliable for evaluating the molecular weights of such neutral complexes. If the parent ion is not evident on the mass spectrum, the use of vapor-phase osmometry may be required to determine the molecular weight of the complex.
(83) Holderegger, R.; Venanzi, L. M. *Helv. Chim. Acta* **1979**, *62* (7), 2154.
(84) Bigorgne, M.; Poilblanc, R.; Pankowski, M. *Spectrochim. Acta* **1970**, *26A*, 1217.
(85) Verkade, J. G. Coord. *Chem. Rev.* **1972/1973**, *9*, 1.
(86) Holderegger, R.; Venanzi, L. M.; Bachechi, F.; Mura, P.; Zambonelli, L. *Helv. Chim. Acta* **1979**, *62* (7), 2159.
(87) Mingos, D. M. P.; Sherman, D. J.; Williams, I. D. *Transition Met. Chem.* **1987**, *12*, 493.
(88) Gray, G. M.; Duffey, C. H. *Organometallics* **1994**, *13* (5), 1542.
(89) Gray, G. M.; Duffey, C. H. *Organometallics* **1995**, *14* (1), 245.
(90) Duffey C. H.; Lake C. H.; Gray, G. M. *Organometallics* **1998**, *17* (16), 3550.
(91) Gray, G. M.; Varshney, A.; Duffey, C. H. *Organometallics* **1995**, *14* (1), 238.
(92) Shimizu, S.; Shirakawa, S.; Sasaki, Y.; Hirai, C. *Angew. Chem., Int. Ed.* **2000**, *39* (7), 1256.
(93) Buergi, H.-B.; Murray-Rust, J.; Camalli, M.; Caruso, F.; Venanzi, L. M. *Helv. Chim. Acta* **1989**, *72*, 1293.
(94) Bauer, E. B.; Ruwwe, J.; Martin-Alvarez, J. M.; Peters, T. B.; Bohling, J. C.; Hampel, F. A.; Szafert, S.; Lis, T.; Gladysz, J. A. *Chem. Commun.* **2000**, 2261.
(95) Ulman, M.; Grubbs, R. H. *J. Org. Chem.* **1999**, *64*, 7202.
(96) Leising, R. A.; Gryzbowski, J. J.; Takeuchi, K. J. *Inorg. Chem.* **1988**, *27* (6), 1020.
(97) Perez, W. J.; Lake, C. H.; See, R. F.; Toomey, L. M.; Churchill, M. R.; Takeuchi, K. J.; Radano, C. P.; Boyko, W. J.; Bessel, C. A. *J. Chem. Soc., Dalton Trans.* **1999**, 2281.
(98) Bruner, H.; Bailar, J. C., Jr. *Inorg. Chem.* **1973**, *12* (7), 1465.
(99) Evans, G. O.; Pittman, C. U., Jr.; McMillan, R.; Beach, R. T.; Jones, R. *J. Organomet. Chem.* **1974**, *67*, 295.
(100) (a) Pignolet, L. M. *Homogeneous Catalysis with Metal Phosphine Complexes*; Perseus Books: Cambridge, 1983. (b) McAuliffe, C. A. *Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands*; Wiley: New York, 1973. (c) *Catalytic Aspects of Metal Phosphine Complexes*; Alyea, E. C.; Meek, D. W. Eds.; ACS Advances in Chemistry Series 196; American Chemical Society: Washington, DC, 1982. (d) McAuliffe, C. A.; Levason, W. *Phosphine, Arsine, and Stibine Complexes of the Transition Elements*; Elsevier Science: New York, 1978. (e) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(101) Venanzi, L. M. *Appl. Chem.* **1980**, *52*, 1117.
(102) Hill, W. E.; Minahan, D. M. A.; Taylor, J. G.; McAuliffe, C. A. *J. Chem. Soc., Perkin Trans. 2* **1982**, 327.
(103) Levason, W.; McAuliffe, C. A. *Advances in Inorganic Chemistry and Radiochemistry*; Emeleus, H. J., Sharpe, A. G., Eds.; Academic Press: New York, 1972; Vol. 14, p 173.

CR990346W