Synthesis of [^{15}N,^{18}O]NH$_2$OH·HCl. A magnetic stirring bar and finely powdered Na^{15}N^{18}O$_2$ (24% ^{15}N, 32% ^{18}O; 3.45 g, 50 mmol) were placed in an oven-dried 200-mL flask. This was flushed with nitrogen, and a rubber septum and a reflux condenser were attached. After 75 mL of dry THF was introduced, the addition of BMS (9.2 M, 11.2 mL, 103 mmol) was started at room temperature. The addition of BMS was stopped after every 5–10 drops in order to allow the reaction to proceed. The progress of the reaction was apparent from the smooth evolution of bubbles and a gentle refluxing of methyl sulfide on the walls of the flask. (It is important to add BMS slowly. In one of the trial experiments, violent frothing occurred when the addition was more rapid.) The addition of BMS was then continued dropwise to maintain a gentle refluxing of methyl sulfide. Stirring was continued overnight under a nitrogen atmosphere. The reaction mixture was cooled in an ice–salt mixture and hydrolyzed carefully with 20 mL of water, and the borohydride was decomposed by the addition of 20 mL of 6 N HCl, with care taken not to allow the temperature to rise above 5 °C. After the mixture was stirred for 20 min, acetone (5 mL) was added and stirring was continued for 10 min. The pH of the mixture was then brought to 8–9 by the careful addition of NaOH solution, and the reaction mixture was saturated with NaCl. The organic layer was separated, and the aqueous layer was washed three times with diethyl ether. The ether extract and the organic layer were mixed together and dried with CaCl$_2$, and the solvent was evaporated to obtain [^{15}N,^{18}O]acetoxime (3.03 g, 83%; 24% ^{15}N, 32% ^{18}O).

The labeled acetoxime (3 g) in a 50-mL flask was refluxed gently with 30 mL of 2 N HCl for 1 h, and the mixture was then distilled at atmospheric pressure. When the distillate was free of acetone, distillation was continued at reduced pressure until the volume was reduced to 3 mL. This solution was cooled in an ice–salt mixture, whereupon colorless crystals of hydroxylamine hydrochloride appeared. This was then lyophilized to obtain dry, crystalline ^{15}NH$_2$^{18}OH·HCl (2.78 g; 24% ^{15}N, 32% ^{18}O), which was then recrystallized from absolute alcohol: yield 2.55 g (74%); mp 155 °C.

In separate experiments, the reduction of sodium nitrite suspended in THF was performed with use of BH$_3$·THF (1 M) as well as BMS (2 M) in THF; the yield of acetoxime was about the same in all the cases. However, it was necessary to conduct reductions with BH$_3$·THF at 0 °C because lower yields resulted when the reaction was done at room temperature.

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Correlations of ^{195}Pt–^{31}P Coupling Constants with Platinum–Ligand and Platinum–Platinum Bond Lengths in Platinum(I) Dimers and in Related Platinum(II) Complexes[1]

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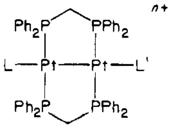
Dimeric platinum(I) complexes with bridging bis(diphenylphosphino)methane ligands, [Pt$_2$(μ-dppm)$_2$(L)L′]$^{n+}$, or, as abbreviated here, [L- -L′]$^{n+}$, are now quite numerous.[2-7] Their availability presents a rare opportunity to study the physical properties and reactivity of a metal–metal bond as a function of the ligands trans to it with a minimum of competing variables. For example, the reactions of diazomethane with various [L- -L′]$^{n+}$ complexes, forming methylene-bridged A-frames, vary considerably in rate[8] and even change mechanism[9] as a function of the terminal ligands. Similarly, the reactions of *cyclo*-octasulfur with various [L- -L′]$^{n+}$ complexes, forming sulfido-bridged A-frames, have been studied systematically.[9,10] We now wish to report several interesting trends of Pt–P coupling constants with Pt–L and Pt–Pt bond lengths in Pt(I) dimers, [L- -L′]$^{n+}$, and structurally related Pt(II) complexes, *trans*-Pt(PR$_3$)$_2$(L)L′. Some of these trends were suggested earlier, and we merely provide further supportive evidence from more recent data.



[L- -L′]$^{n+}$

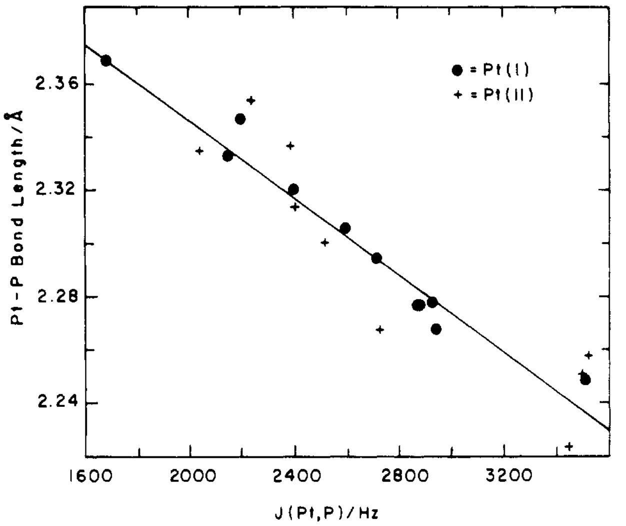


Figure 1. Pt–P bond length vs. ^1J(Pt,P) for dppm-bridged Pt(I) dimers (●) and Pt(II) compleces (+). The least-squares slope is extrapolated to ^1J(Pt$_A$,P$_T$) = 1680 Hz to estimate the bond distance in [Pt$_2$(μ-dppm)$_2$(PPh$_3$)$_2$]$^{2+}$.

Table I. Selected Pt–Cl Bond Lengths in *trans*-[Pt(Y)Cl(PR$_3$)$_2$]$^{n+}$

complex	Y–	Pt–Cl/Å	ref
trans-[PtH(PEtPh$_2$)$_2$Cl]	H–	2.422	12
[Pt$_2$(μ-dppm)$_2$Cl$_2$]	Cl–Pt–	2.405	13
[Pt$_2$(μ-dppm)$_2$Cl(PPh$_3$)]$^+$	Ph$_3$P–Pt–	2.403	7
[Pt$_2$(μ-dppm)$_2$(CO)Cl]$^+$	OC–Pt–	2.384	15
[Pt(PEt$_3$)$_3$Cl]$^+$	Et$_3$P–	2.366	16
trans-[Pt(PEt$_3$)$_2$Cl$_2$]	Cl–	2.249	17

Results and Discussion

Trans Influence of the dppm-Bridged Pt–Pt Bond. The influence[11] of trans ligands on ground-state properties can extend to the trans metal–ligand bond distance, the vibrational frequency or force constant, the NMR coupling constant between the metal and the trans-ligand donor atom, and a host of other parameters. As the trans influence of a ligand increases, the M–L$_{\text{trans}}$ bond

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[1] Based in part on: Blau, Reed J. Ph.D. Thesis, Iowa State University, 1985.

[2] Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1977**, 951.

[3] Brown, M. P.; Puddephatt, R. J.; Rashidi, M.; Seddon, K. R. *J. Chem. Soc., Dalton Trans.* **1978**, 1540.

[4] Brown, M. P.; Franklin, S. J.; Puddephatt, R. J.; Thomson, M. A.; Seddon, K. R. *J. Organomet. Chem.* **1979**, *179*, 281.

[5] Brown, M. P.; Fisher, J. R.; Hill, R. H.; Puddephatt, R. J.; Seddon, K. R. *Inorg. Chem.* **1981**, *20*, 3516.

[6] Azam, K. A.; Brown, M. P.; Hill, R. J.; Puddephatt, R. J.; Yavari, A. *Organometallics* **1984**, *3*, 697.

[7] Blau, R. J.; Espenson, J. H.; Kim, S.; Jacobson, R. A. *Inorg. Chem.* **1986**, *25*, 757.

[8] Muralidharan, S.; Espenson, J. H. *Inorg. Chem.* **1983**, *22*, 2786.

[9] Muralidharan, S.; Espenson, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 8104.

[10] Muralidharan, S.; Ross, S. A.; Espenson, J. H., unpublished results.

[11] Purcell, K. F.; Kotz, J. C. "Inorganic Chemistry"; W. B. Saunders: Philadelphia, 1977; pp 702–706.

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Table II. Platinum–Phosphorus Coupling Constants (Hz) for $[Pt_2(\mu\text{-dppm})_2L(PR_3)]^{n+}$ Complexes[a]

complexes	^1J-(Pt_A,P_A)	^1J-(Pt_R,P_R)	^1J-(Pt_A,P_T)	^2J-(Pt_R,P_T)	ref
$[I\text{--}PPh_3]^+$	2881	2843	2200	1290	7
$[Cl\text{--}dppm]^+$	2921	2872	2146	1270	7
$[Cl\text{--}PPh_3]^+$	2876	2894	2186	1232	7
$[PPh_3\text{--}PPh_3]^{2+}$	2800		1680	1008	4
$[PMePh_2\text{--}PMePh_2]^{2+}$	2870		1914	750	4
$[PMe_2Ph\text{--}PMe_2Ph]^{2+}$	2840		1938	650	4
$[H\text{--}dppm]^+$	2880	3510	2190	620	5
$[H\text{--}PPh_3]^+$	2894	3532	2181	596	5
$[H\text{--}PMePh_2]^+$	2850	3484	2162	592	5
$[H\text{--}PMe_2Ph]^+$	2884	3470	2188	576	5
$[Me\text{--}PPh_3]^+$	2976	3510	2040	490	6
$[Me\text{--}PMe_2Ph]^+$	2960	3510	2054	476	6
$[Me\text{--}dppm]^+$	2970	3550	2020	435	6

[a] Solvent was CD_2Cl_2 in all cases; the structural formula for ligand positions is

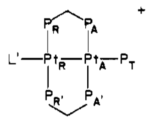

Table III. Selected Pt–P Bond Lengths and ^1J(Pt,P) Values in *trans*-$[Pt(PR'_3)_2(PR_3)(Y)]^{n+}$

complex	Y–	Pt–PR_3/ Å	^1J-(Pt,P_Y)/ Hz	ref
trans-$[PtH(P(cy)_3)_2(PPh_3)]^{+}$[a]	H–	2.359		18
$[H\text{--}dppm]^+$	H–Pt–	2.347	2190	19
$[PtH(PEt_3)_3]^+$	H–	2.335	2037	16
$[Cl\text{--}PPh_3]^+$	Cl–Pt–	2.333	2146	7
$[Pt(PEt_3)_3Cl]^+$	Cl–	2.251	3499	16
$[Pt(PEt_3)_3F]^+$	F–	2.224	3455	16

[a] $P(cy)_3 = P(C_6H_{11})_3$.

length increases. For example, X-ray crystallographic data[12,13,15–17] suggest that the trans-influence order[11] is

$$\sigma\text{-}R^- \simeq H^- \geq PR_3 > CO \simeq Cl^-$$

When the Pt–Cl bond lengths of dppm-bridged Pt(I) dimers containing Cl^- bound trans to the Pt–Pt bond are compared with other Pt–Cl bond distances (see Table I), it becomes apparent that the trans influence of a dppm-bridged Pt–Pt bond lies between that of a hydride and a tertiary phosphine but is more like the former.

As the metal–ligand bond distance increases, the $^1J(M,L_{trans})$ value decreases.[17] The values of $^1J(Pt_A,P_A)$ and $^1J(Pt_A,P_T)$, to use the designations shown in Table II, remain fairly constant in the series of Pt(I) complexes. The constancy of these coupling constants suggests that the Pt–P bond lengths remain constant within each group but are significantly lengthened when phosphorus is trans to the Pt–Pt bond. Indeed, from the ^1J(Pt,P) values and Pt–PR_3 bond distances[7,16,18,19] in Pt(I) and Pt(II) complexes of the *trans*-$[Pt(PR'_3)_2(PR_3)(Y)]^{n+}$ type (Table III), the following trans-influence order can be constructed:

$$H^- \simeq L\text{–}Pt >> Cl^- > F^-$$

As in the trans-influence order generated from Pt–Cl bond distances, a Pt–Pt bond has a trans influence resembling that of H^-. Estimates of the trans influence of a dppm-bridged Pt–Pt bond have been made elsewhere.[5,6]

Table IV. The "Cis Effect" of Substituents on Pt–P Bond Lengths and ^1J(Pt,P) in *trans*-$[Pt(PR_3)_2(X)(Y)]^{n+}$

complex	X–Pt–Y	Pt–P/Å	^1J(Pt,P)/Hz	ref
$[Pt(PEt_3)_3Cl]^+$	P–Pt–Cl	2.354	2233	16
$[Pt(PEt_3)_3F]^+$	P–Pt–F	2.337	2382	16
$[CO\text{--}CO]^{2+}$	Pt–Pt–CO	2.320	2390	4, 21
trans-$[Pt(PEt_3)_2Cl_2]$	Cl–Pt–Cl	2.314	2400	17
$[Cl\text{--}CO]^+$	Pt–Pt–CO	2.306	2591	15
$[PtH(PEt_3)_3]^+$	H–Pt–P	2.301	2515	16
$[Cl\text{--}CO]^+$	Pt–Pt–Cl	2.295	2711	15
$[Cl\text{--}PPh_3]^+$	Pt–Pt–P	2.278	2921	7
$[H\text{--}dppm]^+$	Pt–Pt–P	2.277	2880	5, 19
$[Cl\text{--}PPh_3P]^+$	Pt–Pt–Cl	2.277	2872	7
trans-$[PtH(PEtPh_2)_2Cl]$	H–Pt–Cl	2.268	2723	12
$[Cl\text{--}Cl]$	Pt–Pt–Cl	2.268	2936	2, 13
$[H\text{--}dppm]^+$	H–Pt–Pt	2.249	3510	5, 19

Table V. Pt–Pt Bond Lengths and ^{31}P–^{195}Pt NMR Coupling Constants[a]

complex	Pt–Pt/Å	$^1J(Pt,P)_{cis}$/ Hz	$^2J(Pt,P)_{trans}$/ Hz	ref
$[Cl\text{--}CO]^+$	2.620	−62, −92	na	15
$[CO\text{--}CO]^{2+}$	2.642	−96	na	4, 21
$[Cl\text{--}Cl]$	2.651	−136	na	2, 13
$[Cl\text{--}PPh_3]^+$	2.665	±37, ±142	1232	7
$[H\text{--}dppm]^+$	2.765	nr	620	5, 19

[a] Legend: na = not applicable; nr = not reported.

Estimation of a Pt–P Bond Distance. The relative insensitivity of $^1J(Pt_A,P_T)$ (Table II) to the nature of the terminal ligand L' bound to Pt_R does not extend to $[PR_3\text{--}PR_3]^{2+}$ complexes, however, where steric influences lengthen the Pt–P bond and thus decrease $^1J(Pt_A,P_T)$. In $[PPh_3\text{--}PPh_3]^{2+}$, the $^1J(Pt_A,P_T)$ value of 1680 Hz is even smaller than the ^1J(Pt,P) value observed for a phosphine trans to a methyl (e.g., 1719 Hz in *cis*-$[PtMe(PEt_3)_2Cl]$).[16] A correlation between Pt–P bond length and ^1J(Pt,P) has been reported for Pt(II) and Pt(IV) complexes.[20] The data for Pt(II) and Pt(I) complexes in Tables III and IV were used to construct a plot of Pt–P bond length[2–5,12,13,15–21] vs. ^1J(Pt,P). From both correlations, the Pt–P_T bond distance in $[PPh_3\text{--}PPh_3]^{2+}$ is estimated to be 2.37 ± 0.02 Å. This is significantly longer than the 2.333 and 2.347 Å found in $[Cl\text{--}PPh_3]^+$[14] and $[H\text{--}dppm]^+$, respectively. The long and presumably weak Pt–PPh_3 bond found in $[PPh_3\text{--}PPh_3]^{2+}$ is consistent with the dissociative character inherent in its reactions[13,22] and with the observation that chair–boat interconversion is facile.[7] Note that the data for Pt(I) dimers and Pt(II) complexes lie on a single line; correlation of data for Pt(IV) and Pt(II) complexes had previously been noted.[20]

^2J(Pt,P) and Pt–Pt Bond Strength. Despite the insensitivity of $^1J(Pt_A,P_T)$ to L', $^2J(Pt_R,P_T)_{trans}$ values are very sensitive to the nature of L' and follow the trans-influence order (see Table II)

$$Me^- > H^- > PMe_2Ph > PMePh_2 > PPh_3 > X^-$$

The Pt_A–P_T bond distances in $[H\text{--}dppm]^+$ and $[Cl\text{--}PPh_3]^+$ are almost identical (2.347 and 2.333 Å), and so $^1J(Pt_A,P_T)$ would be expected to vary little between the two complexes. Because the corresponding Pt–Pt bond lengths vary considerably (2.769

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[12] Eisenberg, R.; Ibers, J. A. *Inorg. Chem.* **1965**, *4*, 773.

[13] Manojlovic-Muir, Lj.; Muir, K. W.; Solomun, T. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *35*, 1237.

[14] Cairns, M. A.; Dixon, K. R.; Rivett, G. A. *J. Organomet. Chem.* **1979**, *171*, 373.

[15] Manojlovic-Muir, Lj.; Muir, K. W. *J. Organomet. Chem.* **1979**, *179*, 479.

[16] Russell, D. R.; Muhammed, M. A.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1737.

[17] Pregosin, P. S.; Kunz, R. W. *NMR: Basic Princ. Prog. 16*, 179.

[18] Clark, H. C.; Dymarski, M. J.; Oliver, J. D. *J. Organomet. Chem.* **1978**, *154*, C40.

[19] Manojlovic-Muir, Lj.; Muir, K. W. *J. Organomet. Chem.* **1981**, *219*, 129.

[20] Pidcock, A. *Adv. Chem. Ser.* **1982**, *No. 196*, 1 and references therein. See also: Mather, G. G.; Pidcock, A.; Rapsey, G. J. N. *J. Chem. Soc., Dalton Trans.* **1973**, 2095.

[21] Fisher, J. R.; Mills, A. J.; Sumner, S.; Brown, M. P.; Thomson, M. A.; Puddaphatt, R. J.; Frew, A. A.; Manojlovic-Muir, Lj.; Muir, K. W. *Organometallics* **1982**, *1*, 1421.

[22] Brown, M. P.; Fisher, J. R.; Franklin, S. J.; Puddephatt, R. J.; Seddon, K. R. *J. Organomet. Chem.* **1978**, *161*, C46.

and 2.665 Å) and the $^2J(Pt_R,P_T)$ values decrease dramatically with increasing Pt–Pt bond length (620 and 1232 Hz), the size of $^2J(Pt_R,P_T)_{trans}$ appears to be a good indicator of Pt–Pt bond strength. This correlation of $^2J(Pt,P)_{trans}$ with Pt–Pt bond distances in $[L'{-}{-}PR_3]^{n+}$ suggests that the Pt–Pt bond is weakened with increasing trans influence of L′. The Pt–Pt bond distances of other $[L{-}{-}L']^{n+}$ complexes (L $\neq$ PR_3) for which crystal structures have been solved also tend to support this correlation (see Table V) but suggest that other factors may also affect the Pt–Pt bond length (trans influence: CO $\simeq$ Cl^-).

A good correlation of Pt–Pt bond distance with not only $^2J(Pt,P)_{trans}$ but also $^2J(Pt,P)_{cis}$ is observed. It was proposed that the size of $^2J(Pt,P)_{cis}$ in $[L{-}{-}L']^{n+}$ should be a function of Pt–Pt bond strength.[23] Since then, the crystal structures of $[CO{-}{-}CO]^{2+}$[21] $[Cl{-}{-}PPh_3]^{+}$[7] and $[H{-}{-}dppm]^{+}$[19] (see Table V) have been solved. The $^2J(Pt,P)_{cis}$ value for $[CO{-}{-}CO]^{2+}$ fits well in the trend of decreasing $^2J(Pt,P)_{cis}$ with increasing Pt–Pt bond length as do the values for $[Cl{-}{-}PPh_3]^+$ if one assumes the coupling constants have negative signs.

$^2J(Pt,P)_{cis}$ and $^2J(Pt,P)_{trans}$ values tend to complement each other as a measure of Pt–Pt bond strength. Although the cis coupling constants should be observed in all Pt(I) dimers of this type, problems are often encountered because it is difficult to determine the sign of these relatively small coupling constants and because the cis satellites are not always well separated from the central resonance. These problems are magnified in highly coupled systems such as complexes containing terminally bound phosphines (e.g., in $[H{-}{-}dppm]^+$), where correlation of $^2J(Pt,P)_{trans}$ with Pt–Pt bond length appears to be more useful because of its larger magnitude and greater sensitivity. Therefore, although neither type of coupling constant is observed in all $[L{-}{-}L']^{n+}$ complexes due to the nature of L and L′ (e.g., $^2J(Pt,P)_{trans}$) or experimental limitations (e.g., $^2J(Pt,P)_{cis}$), at least one of these constants is observed for practically all [L- -L′] complexes.

Cis Influence in Pt(I) Dimers. A general conclusion from efforts[20] to find a correlation between the strength of a metal–ligand bond and the nature of the cis ligands is that three factors are of comparable importance: σ effects, π effects, and steric factors. (This is in contrast with the trans influence, where the first appears to dominate.) When indirect (i.e., two- or three-bond) coupling constants are used as a measure of the cis influence, cis and trans influences appear to be inversely correlated. Direct (i.e., one-bond) coupling constants are, however, markedly reduced by π bonding to a cis ligand.[14] A cis-influence series, derived[14] from values of $^1J(Pt,P)$ for Pt(II) complexes, shows that those ligands with large trans *and* cis influences are those that are π acceptors:

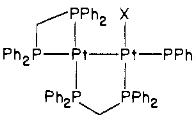
$$CO > P(OR)_3 > CN^- > PEt_3 > I^- > Cl^- > H^- > Me$$

The series of closely related Pt(I) dimers found in Table II follow this trend. The values of $^1J(Pt_R,P_R)$ in $[Ph_3P{-}{-}L]^{n+}$ according to cis influence are as follows: L = PPh_3 (2800 Hz) > I (2843) > Cl (2894) > H (3532) $\approx$ Me (3510).

The carbonyl ligand, a strong π acceptor but only a moderate σ donor, has the highest cis influence but an intermediate trans influence in accord with these generalizations. This is illustrated by the Pt–P bond distances and $^1J(Pt,P)$ coupling constants in Table IV for the series $[CO{-}{-}CO]^{2+}$ (d = 2.320 Å, J = 2390 Hz), $[Cl{-}{-}CO]^+$ (2.295 and 2.306, 2591 and 2711), $[Cl{-}{-}PPh_3]^+$ (2.277, 2872), and [Cl- -Cl] (2.268, 2936). It is evident that the Pt–P bonds cis to CO are weakened considerably by its π-accepting ability. Even a cis-located CO three bonds away from the phosphorus in question can compete effectively with it for potential π-electron density. The three-bond cis influence through the Pt–Pt bond parallels that for the normal two-bond effect, CO > PPh_3 > Cl in $[L{-}{-}Cl]^{n+}$.

A dppm-bridged Pt–Pt bond has a cis influence, as well as a trans influence, very similar to that of a hydride. That is illustrated by data in Table IV for the series of *trans*-$[Pt(PR_3)_2(L)Cl]$ complexes with L = PPh_3 (d = 2.354 Å, $^1J_{Pt,P}$ = 2233 Hz), Cl (2.314, 2400), L′–Pt (2.280, 2838; average of three compounds), and H (2.268, 2723). The low cis influences of hydride and of Pt(I) are due in part to their inability to accept π-electron density from the adjacent Pt center. In fact, the shortest Pt–P bond and the largest coupling constant occur when both Pt(I) and hydride are cis to Pt–P bonds.

Summary. Because of the wide range of values possible for platinum–phosphorus coupling constants, they have proven in the past[17] and continue to be sensitive indicators of not only the structure and stereochemistry of platinum phosphine complexes (e.g., in the structural determination of A)[23] but also the electronic and steric influences of the ligands in such complexes.



A

These results and correlation suggest the following: (1) the Pt–Pt bond in $[L{-}{-}L']^{n+}$ has trans and cis influence similar to those of a hydride; (2) because of the sensitivity of $^1J(Pt,P)$ to Pt–P bond length, a value for the Pt–PPh_3 bond length in $[PPh_3{-}{-}PPh_3]^{2+}$ can be estimated; (3) both $^2J(Pt,P)_{cis}$ and $^2J(Pt,P)_{trans}$ are sensitive to the Pt–Pt bond strength in complexes containing the $[Pt_2(\mu\text{-dppm})_2]^{2+}$ core; (4) ligands with a large trans influence appear to weaken the Pt–P bond when they are bound trans to it; (5) the cis influence of ligands in Pt(I) dimers parallels that in Pt(II) monomers and can be transmitted through three bonds via the Pt–Pt bond in the dimers; (6) the Pt–Pt bond exhibits a very low cis influence.

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Intramolecular Ligand Rearrangements in Anionic Group 6 Metal Pentacarbonyl Hydride Derivatives

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Several research groups have reported ligand rearrangements in six-coordinate, low-valent metal carbonyl derivatives that occur without loss of bound ligands, i.e., via intramolecular pathways.[1] Cis $\rightleftharpoons$ trans isomerization processes involving $M(CO)_4LL'$ complexes comprise the bulk of the instances investigated. In general, these processes are thermodynamically driven due to the electronic and/or steric site preferences of the noncarbonyl ligands L and L′. Earlier we examined *intramolecular* ligand rearrangements in phosphine and phosphite derivatives of Cr and W pentacarbonyl (eq 1) that have been stereoselectively labeled with ^{13}C-substituted

$$cis\text{-}M(CO)_4(^{13}CO)L \rightleftharpoons trans\text{-}M(CO)_4(^{13}CO)L \qquad (1)$$

carbon monoxide, where there is no thermodynamic driving force for isomerization.[2,3] Similarly, Dombek and Angelici have studied

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[1] (a) Vancea, L.; Pomeroy, R. K.; Graham, W. A. G. *J.Am. Chem. Soc.* **1976**, *98*, 1407. (b) Pomeroy, R. K.; Vancea, L.; Calhoun, H. P.; Graham, W. A. G. *Inorg. Chem.* **1977**, *16*, 1508 and references therein. (c) Fischer, H.; Fischer, E. O.; Werner, H. *J. Organomet. Chem.* **1974**, *73*, 331. (d) Darensbourg, D. J.; Kump, R. L. *Inorg. Chem.* **1978**, *17*, 2680. (e) Darensbourg, D. J. *Inorg. Chem.* **1979**, *18*, 14. (f) Dixon, D. T.; Kola, J. C.; Howell, J. A. S. *J. Chem. Soc., Dalton Trans.* **1984**, 1307. (g) Fischer, H.; Motsch, A.; Markel, R.; Ackermann, K. *Organometallics* **1985**, *4*, 726. (h) Nubel, P. O.; Brown, T. L. *J. Am. Chem. Soc.* **1984**, *106*, 644.

0020-1669/86/1325-0880$01.50/0