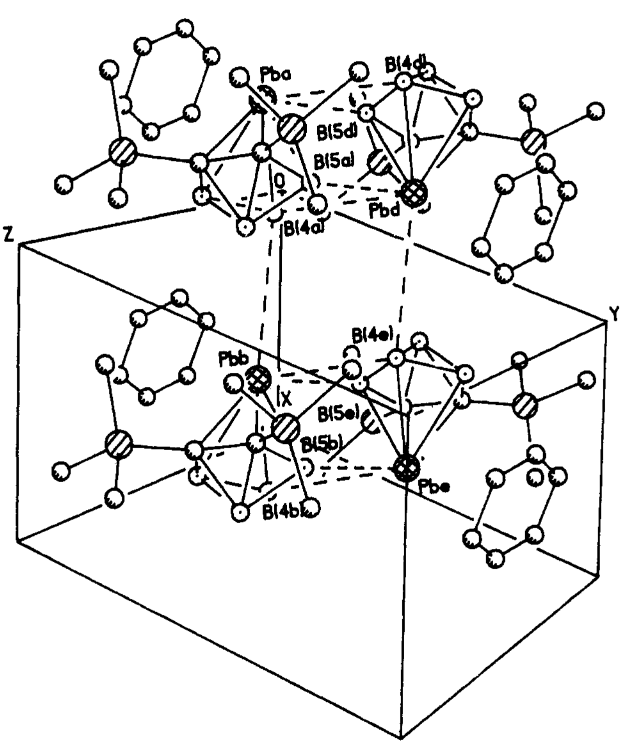

Figure 1. The crystal packing diagram showing the extended chain network of $[closo\text{-}1\text{-}Pb\text{-}2,3\text{-}(SiMe_3)_2\text{-}2,3\text{-}C_2B_4H_4]_2$ molecular clusters with benzene molecules of crystallization. The intermolecular Pb(a)-Pb(d), Pb(a)-B(4d), Pb(a)-B(5d), Pb(b)-B(4a), and Pb(b)-B(5a) distances are 4.165 (14), 3.375 (15), 3.195 (16), 3.868 (16), and 4.966 (20) Å, respectively.

However, the solid-state structure of $(Me_5C_5)_2Pb$ was found to be monomeric and slipped.[14] Even the shortest Pb-C distance of 2.69 (1) Å in $(Me_5C_5)_2Pb$ is considerably longer than the longest Pb-cage distance [Pb-C(2) = 2.634 (14) Å] found for the plumbacarborane II. Therefore, it can be stated that the Pb atom is more covalently bonded with the carborane cage than with the cyclopentadienyl ring.

The symmetric structure of the plumbacarborane is quite surprising. At present, it is not known how much the unusual dimeric cluster formation affects the structure of a PbC_2B_4 unit or whether this dimer exists in solution. This and other aspects of the chemistry of *closo*-plumbacarboranes and their derivatives are currently underway in our laboratories.

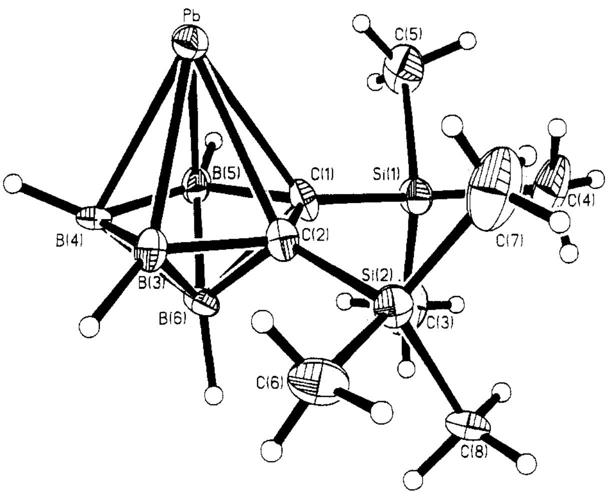

Figure 2. Structure of one of the plumbacarboranes in Figure 1 showing the atom-numbering scheme and thermal ellipsoids at the 30% probability level. Pertinent parameters include Pb-C(1) = 2.582 (17), Pb-C(2) = 2.634 (14), Pb-B(3) = 2.601 (16), Pb-B(4) = 2.579 (17), and Pb-B(5) = 2.520 (20) Å.

Acknowledgment. This work was supported by grants from the National Science Foundation (CHE-8800328), the Robert A. Welch Foundation (N-1016), and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Tables of positional and thermal parameters (Table S1), bond distances (Table S2), bond angles (Table S3), torsion angles (Table S4), anisotropic temperature factors (Table S5), and H-atom coordinates and isotropic displacement parameters (Table S6) (7 pages); a listing of observed and calculated structure factors (Table S7) (9 pages). Ordering information is given on any current masthead page.

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(11) Crystal and Experimental Data. Suitable colorless needle-shaped crystals of II ($C_8H_{22}B_4Si_2Pb\cdot{}^1/_2C_6H_6$, fw 463.9) were grown in C_6H_6 solution. Since the crystals changed to opaque-white upon brief exposure to air, they were coated with an epoxy resin. Data were collected at 233 K, using an automatic Nicolet R3m/V diffractometer, Mo Kα radiation. The space group is $P\bar{1}$ with a = 6.409 (6) Å, b = 10.068 (11) Å, c = 14.86 (2) Å, α = 79.5 (1)°, β = 88.3 (1)°, γ = 74.13 (9)°, U = 907 (2) Å^3, Z = 2, and d_{calcd} = 1.70 g cm^{-3}. A total of 2370 independent reflections in the range $3.0 \leq 2\theta \leq 45$ were collected. Three standard reflections collected after every 100 reflections showed ~16% decay of intensity at the end of the data collection. Data were corrected for decay, Lorentz-polarization, and absorption. Structure was solved by direct methods programs used in SHELXTL-Plus (Sheldrick, G. M. *Structure Determination Software Programs*; Nicolet Instrument Corp., Madison, WI, USA, 1988) and subsequent difference Fourier methods. Final full-matrix least-squares refinement (SHELXTL-Plus) using 2077 observed reflections with $F > 6.0\sigma(F)$ converged to R = 0.048 and R_w = 0.050; S = 1.03, $(\Delta/\sigma)_{max}$ = 0.006, and $\Delta\rho_{max,min}$ = 2.14 (close to Pb), -2.18 e/Å^3. All non-H atoms were refined anisotropically, and silyl methyl H atoms were constrained tetrahedrally. The function minimized being $\sum w(|F_o| - |F_c|)^2$, the weight used being $w^{-1} = \sigma(F^2) + 0.0054F^2$. Scattering factors for C, H, B, Si, and Pb were those stored in SHELXTL-Plus.

(12) Almenningen, A.; Haaland, A.; Motzfeldt, T. *J. Organomet. Chem.* **1967**, *7*, 97.

(13) Panattoni, C.; Bombieri, G.; Croatto, U. *Acta Crystallogr.* **1966**, *21*, 823.

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Relative Sign Determination of Phosphorus-Carbon Coupling Constants by 2D Carbon-13 NMR Spectroscopy

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Summary: The two-dimensional COSY-90 technique is shown to be a viable method for determining the relative signs of heteronuclear couplings. In particular the $^2J_{PMC}$ coupling constants for three phosphido-bridged ruthenium complexes, $Ru_2(CO)_6[\mu_2\text{-}\eta^2\text{-}C{\equiv}CCH(CH_3)_2](\mu\text{-}PPh_2)$, $Ru_2(CO)_6[\mu\text{-}CHC(Ph)NEt_3](\mu\text{-}PPh_2)$, and $Ru_2(CO)_6[\mu\text{-}O{=}CCHC(Ph)NEt_2](\mu\text{-}PPh_2)$, have been examined and found to depend on the crystallographic PMC angle.

In assessing the stereochemistry and bonding of a wide range of organometallic complexes, both the magnitude and the relative signs of scalar coupling constants such as $^2J_{PMP}$ and $^2J_{PMC}$ are important. Generally, the assignments for monodentate phosphorus ligands have been made on

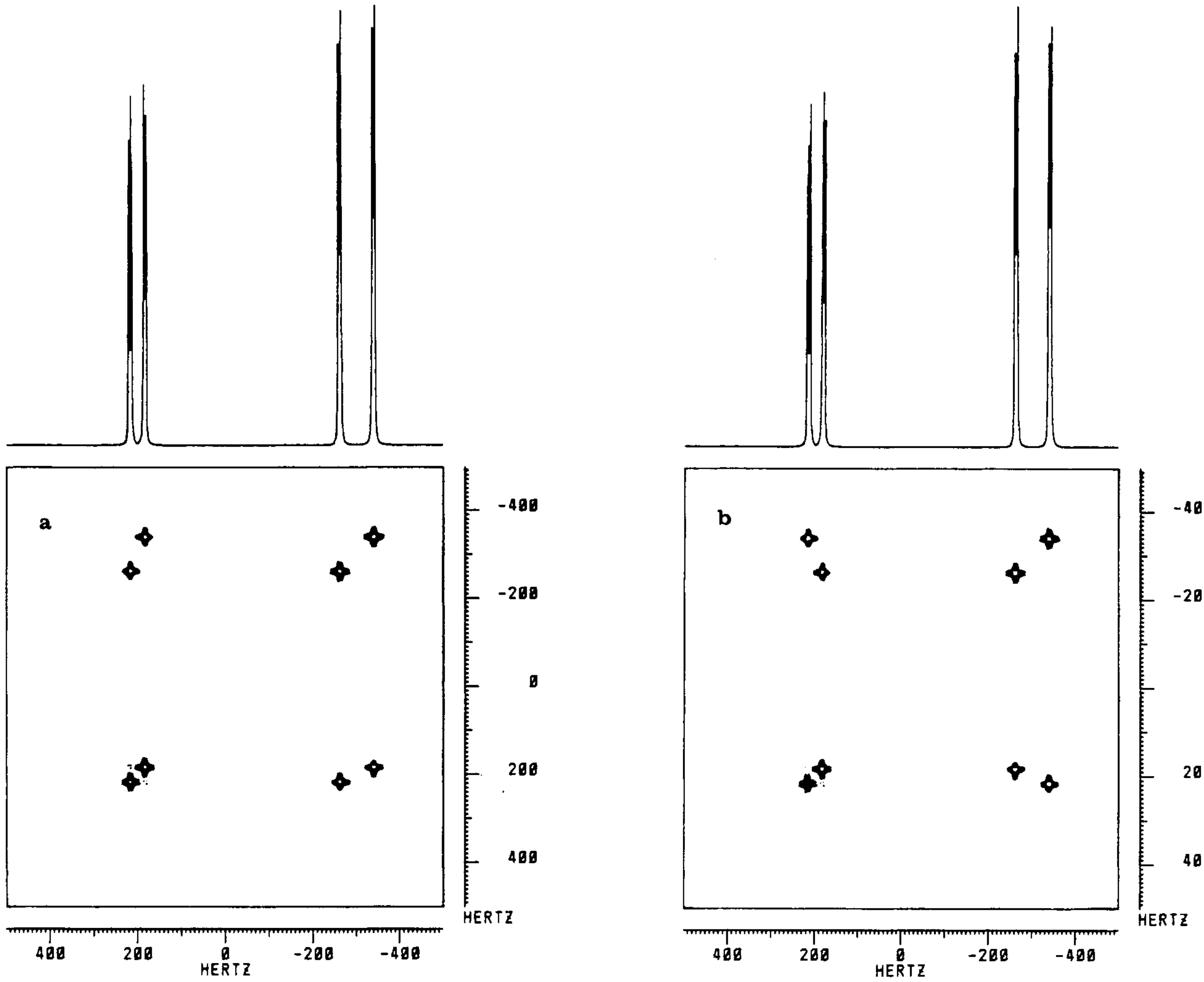

Figure 1. (a) A theoretical contour plot of a SIMPLTN COSY-90 experiment performed for an AMX spin system where X is a heteronuclear spin. J_{AM} = 5 Hz, J_{AX} = 34 Hz, and J_{MX} = 78 Hz. (b) A theoretical contour plot for an AMX system in which J_{AM} = 5 Hz, J_{AX} = 34 Hz, and J_{MX} = −78 Hz.

the basis that $^2J_{PMP}$(trans) is large and positive while $^2J_{PMP}$(cis) is smaller and negative.[1] Although the importance of relative sign information has been recognized, to our knowledge few studies have been concerned with the relative signs of $^2J_{PMC}$ and the potential of these couplings for elucidating stereochemistry lies largely untapped.[2] With the development of 2D NMR experiments, the determination of relative signs has become more accessible. In this communication, we wish to demonstrate the utility of applying the homonuclear shift correlation technique (COSY) to metal carbonyl complexes that contain phosphorus nuclei in order to determine the relative signs of $^2J_{PMC}$ coupling constants.

Conventional NMR spectra of weakly coupled spin systems are not sensitive to the relative signs of spin–spin coupling constants, and special techniques are required for sign determination. The established one-dimensional methods involve the use of second-order features of single-resonance spectra and double- or triple-resonance methods.[3] The multiple-resonance technique is the standard direct method of analysis but usually requires nonstandard probes and electronics. Recently, the reverse two-dimensional NMR technique has been shown to be a viable method for determining the relative signs of heteronuclear systems.[4] This experiment, however, also requires special equipment, and we were interested in a facile method of determining the relative signs of heteronuclear coupling constants that could be performed by using standard technologies. The two-dimensional COSY-45 technique[5] has proven useful for homonuclear ^{31}P AMX spin systems,[6] in which the relative sign information is made available by inspection of the tilt of the off-diagonal peaks and two-dimensional experiments involving ^{13}C carbonyl resonances have recently been shown to be feasible[7] in enriched samples due to efficient spin–lattice

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(1) See for example: (a) *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis: Organic Compounds and Metal Complexes*; Verkade, J. G., Quinn, L. D., Eds.; VCH Publishers: New York, 1987. (b) Pregosin, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Complexes*; Springer-Verlag: Berlin, 1979; Vol. 16. (c) Verkade, J. G. *Coord. Chem. Rev.* **1972**, *9*, 1–106 and references cited therein. It should be stressed that these general trends exist for non-chelating systems.

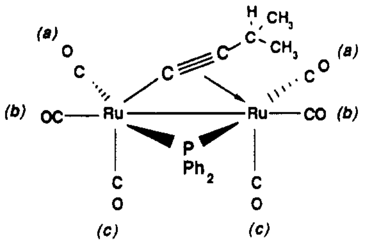
(2) (a) Hommeltoft, S. I.; Cameron, A. D.; Shackelton, T. A.; Fraser, M. E.; Fortier, S.; Baird, M. C. *Organometallics* **1986**, *5*, 1380. (b) Andrews, G. T.; Colquhoun, I. J.; McFarlane, W. *Polyhedron* **1983**, *8*, 783. (c) Colquhoun, I. J.; Grim, S. O.; McFarlane, W.; Mitchell, J. D.; Smith, P. H. *Inorg. Chem.* **1981**, *20*, 2516.

(3) See, for example: (a) McFarlane, W.; Rycroft, D. S. *Annu. Rep. NMR Spectrosc.* **1979**, *9*, 320. (b) Sorensen, S.; Hansen, R. S.; Jakobsen, H. J. *J. Magn. Reson.* **1974**, *14*, 243. (c) Jakobsen, H. J.; Bundgaard, T.; Hansen, R. S. *Mol. Phys.* **1972**, *23*, 197.

(4) Benn, R.; Brenneke, H.; Jurgen, H.; Rufinska, A. *Inorg. Chem.* **1987**, *26*, 2826.

(5) (a) Bax, A. *Two-Dimensional Nuclear Magnetic Resonance in Liquids*; D. Reidel: Dordrecht, 1982 and references cited therein. (b) Bax, A.; Freeman, R. *J. Magn. Reson.* **1981**, *45*, 177.

(6) (a) Fontaine, X. L. R.; Kennedy, J. D.; Shaw, B. L.; Vila, J. M. *J. Chem. Soc., Dalton Trans.* **1987**, 2401. (b) Hutton, W. C. In *Phosphorus-31 NMR, Principles and Applications*; Gorenstein, D. G.; Ed.; Academic: Orlando, 1984.



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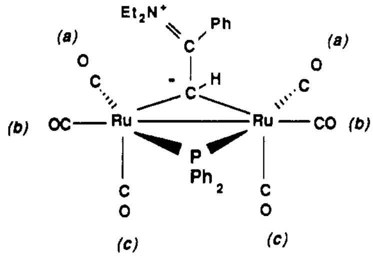

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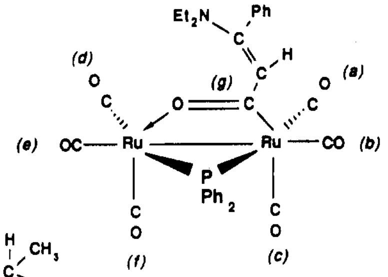

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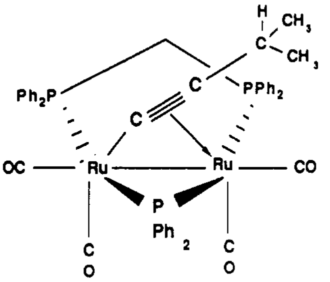
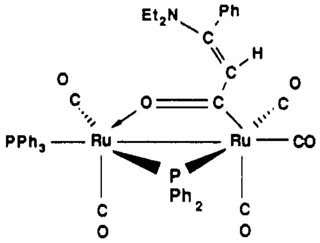


(4)



(5)

relaxation via the chemical shift anisotropy mechanism.[8]

We first examined theoretically the effect of a heteronuclear coupling for an AMX spin system using the SIMPLTN (simulation of pulse and two-dimensional NMR)[9] program. Shown in parts a and b of Figure 1 are the 2D COSY-90 contour plots of a weakly coupled AMX spin system in which the relative sign of the heteronuclear coupling has been changed.[10] Only components with the same heteronuclear spin state show off-diagonal correlations, and thus the relative sign of the heteronuclear coupling can be readily determined from examination of the off-diagonal elements.[11] This result is completely general and will apply to any system which is composed of at least three spins and has homonuclear and heteronuclear couplings.

Shown in Figure 2 is the contour plot of a ^{13}C COSY-90 experiment for the binuclear ruthenium complex $Ru_2(CO)_6[\mu_2\text{-}\eta^2\text{-}C{\equiv}CCH(CH_3)_2](\mu\text{-}PPh_2)$ (1), which by virtue of the σ–π interconversion of the acetylide group, exhibits only three carbonyl resonances in the room-temperature ^{13}C NMR spectrum.[12] The complex is enriched ca. 30% with ^{13}CO in order to observe the $^2J_{CC}$ couplings.[13] From the diagram we can determine that the doublet which has the large phosphorus carbon coupling constant has a sign opposite (presumably positive) to that observed for the two other smaller doublets. Although the assumption of $^2J_{PMX}$(trans) ≫ $^2J_{PMX}$(cis) is frequently used to assign relative PX stereochemistries, there are surprisingly few cases in which the cis and trans ligands can be unequivocally identified by alternate methods.[14] In the present case, however, there is very strong evidence that the large

Table I. X-ray Crystal Data and ^{13}C NMR Shift Assignments for Complexes 1–3

complex	PMC angle	ref	$\delta^{b,c}$	$^2J_{PMC}{}^d$	assignt
$Ru_2(CO)_6[\mu_2\text{-}\eta^2\text{-}C{\equiv}CCH(CH_3)_2](\mu\text{-}PPh_2)$	153^a	12	195.7	73.8	CO(a)
	104^a		194.5	−5.8	CO(b)
	92^a		197.5	−12.0	CO(c)
$Ru_2(CO)_6[\mu\text{-}CHC(Ph)NEt_2](\mu_2\text{-}PPh_2)$	147^a	16	203.3	59.5	CO(a)
	110^a		199.4	−2	CO(b)
	94^a		204.1	−10.7	CO(c)
$Ru_2(CO)_6[\mu\text{-}O{=}CCHC(Ph)NEt_2](\mu\text{-}PPh_3)$	150.9	16	202.8	55.5	CO(a)
	150.5		201.8	68.3	CO(d)
	102.9		199.4	−4.0	CO(b)
	105.8		192.6	~0	CO(e)
	97.0		200.0	−10.3	CO(c)
	95.3		202.0	−11	CO(f)
	80.1		246.2	−11.4	CO(g)

[a] Average of the two crystallographic PMC angles. [b] Relative to TMS, δ = 0 ppm (CD_2Cl_2). [c] Spectra were acquired for complexes 1, 2, and 3 at 300, 213, and 304 K, respectively. [d] The absolute signs are unknown. We have chosen to assign the large trans coupling constants as positive, following McFarlane et al.[2c]

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(7) (a) Hawkes, G. E.; Lian, L. Y.; Randall, E. W.; Sales, K. D.; Aime, S. *J. Chem. Soc., Dalton Trans.* **1985**, 225. (b) Hawkes, G. E.; Lian, L. Y.; Randall, E. W.; Sales, K. D.; Aime, S. *J. Magn. Reson.* **1985**, *65*, 173.

(8) (a) Hawkes, G. E.; Randall, E. W.; Aime, S.; Osella, D.; Elliott, J. E. *J. Chem. Soc., Dalton Trans.* **1984**, 279. (b) Gleeson, J. W.; Vaughan, R. W. *J. Chem. Phys.* **1983**, *78*, 5384. (c) The T_1 times for the carbonyls in $Ru_2(CO)_6[\mu_2\text{-}\eta^2\text{-}C{\equiv}CCH(CH_3)_2](\mu\text{-}PPh_2)$ are ~5.5 s at 4.7 T (50 MHz for ^{13}C).

(9) Allman, T.; Bain, A. D. *J. Magn. Reson.* **1987**, *86*, 533.

(10) The heteronuclear SIMPLTN program has been used with a normal COSY sequence [P_1–t_1–P_2–acquire] and both pulses set to 90°.

(11) If the high-frequency components of the multiplets correlate, the heteronuclear coupling will be of the same sign to both resonances, whereas high-frequency to low-frequency correlations will imply an opposite sign.

(12) $Ru_2(CO)_6[\mu_2\text{-}\eta^2\text{-}C{\equiv}CCH(CH_3)_2](\mu\text{-}PPh_2)$ (1) was prepared by literature methods, Cherkas, A. A.; Randall, L. H.; MacLaughlin, S. A.; Mott, G. N.; Taylor, N. J.; Carty, A. J. *Organometallics* **1988**, *7*, 969.

(13) The complex was stirred under an atmosphere of 90% enriched carbon monoxide for 48 h. The enrichment level was estimated from the ^{13}C satellites of the ^{31}P NMR spectrum to be approximately 30%. Higher enrichment levels will result in greater intensities in the off-diagonal peaks.

(14) For example in complexes of the type $[Ph_2PCH_2P(R^1R^2)]M(CO)_4$, assignment of the ^{13}CO resonances is made by comparison with the observed coupling constants in $LM(CO)_5$ compounds.[2c]

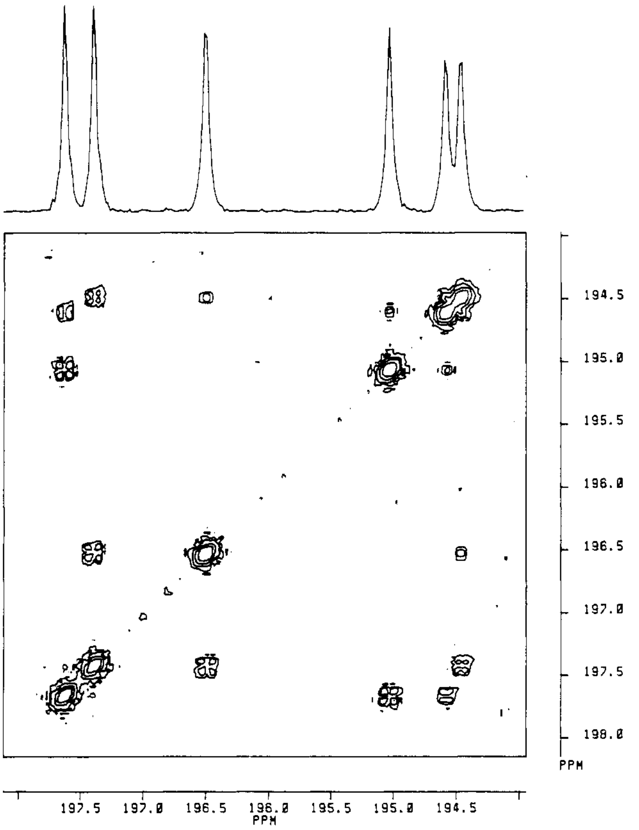

Figure 2. 50-MHz (AC-200) ^{13}C shift-correlated 2D NMR contour plot of $Ru_2(CO)_6[\mu_2\text{-}\eta^2\text{-}C{\equiv}CCH(CH_3)_2](\mu\text{-}PPh_2)$ (1). A ($90°\text{-}t_1\text{-}90°$ free induction decay)$_n$ pulse sequence was used employing a 16-step phase cycle. 16 FID's of 1 K data points were accumulated with a recycle delay of 2.5 s. A total of 256 t_1 values were used with a spectral width of 500 Hz (0.9 Hz/Pt) for a total acquisition time of 4.0 h. The complex was enriched to approximately 30% ^{13}CO in order to exploit the $^2J_{CC}$ coupling.

$^2J_{PMC}$ coupling constants are associated with mutually trans ligands and that the larger of the cis $^2J_{PMC}$ couplings arises from phosphorus and carbon nuclei which lie at approximately 90° to one another.[15]

We have examined the magnitudes and the signs of the $^2J_{PMC}$ coupling constants for three phosphido-bridged ruthenium systems and compared them with the available crystallographic data.[12,16] Our observations have led us to suggest that a viable stereochemical dependence does exist for $^2J_{PMC}$ in these systems (Table I). The coupling constants appear to depend, in part, on the geminal bond angle with a sign inversion occurring near angles of ~110°. In addition, the coupling constants appear to minimize at 90° and maximize at 180°.

Although several factors may influence the size and sign of $^2J_{PMC}$ such as the metal, its oxidation state, and the nature of the ligands, it is important to realize when comparing complexes of a similar nature that when a near zero geminal coupling constant is obtained that this may be the result of a bond angle of 110° not 90°.

The results presented herein demonstrate that the COSY method can lead to a clear determination of the relative signs of coupling constants in heteronuclear systems and that important stereochemical information can be readily obtained. We are presently investigating the application of this technique[17] to related systems in an effort to better understand the fundamental factors which affect geminal coupling constants in metal complexes.

Acknowledgment. We are grateful to NSERC for support of this work in the form of grants (to A.J.C.) and scholarships (to L.H.R. and A.A.C.). We also thank Dr. Alex Bain for many helpful discussions.

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(15) Substitution of two CO ligands of **1** by $Ph_2PCH_2PPh_2$ (dppm) affords a single isomer, $(CO)_2Ru[\mu\text{-}\eta^2\text{-}C{\equiv}CCH(CH_3)_2](\mu\text{-}PPh_2)(\mu\text{-}dppm)Ru(CO)_2$ (**4**) which has been fully characterized by X-ray crystallography. The two CO groups trans to the phosphido bridge in **1** are replaced by phosphorus atoms of the μ-dppm ligand. The ^{13}CO NMR spectrum of **4** [$^{13}C\{^1H\}$ δ 204.4 (m, CO), 201.0 (br s, CO)] at 300 K exhibits only two resonances with small (<6 Hz) $^2J_{PMC}$ couplings, the two resonances with large $^2J_{PMC}$ values in **1** having disappeared. The CO substitution product of **3** with PPh_3, $(PPh_3)(CO)_2Ru(\mu\text{-}O{=}CCHC(Ph)NEt_2)(\mu\text{-}PPh_2)Ru(CO)_3$ (**5**), has also been fully characterized by X-ray diffraction. In **5** the PPh_3 ligand has displaced the CO group trans to the Ru–Ru bond and cis to the phosphido bridge in **3**. The ^{13}C CO NMR spectrum of **5** [$^{13}C\{^1H\}$ δ 252.0 (d, CO, $^2J_{PMC}$ = 10.0 Hz), 206.7 (dd, CO, $^2J_{PMC}$ = 2.5, 75.0 Hz), 206.6 (dd, CO, $^2J_{PMC}$ = 10.0, 8.0 Hz), 204.7 (d, CO, $^2J_{PMC}$ = 53.0 Hz), 201.2 (d, CO, $^2J_{PMC}$ = 11.0 Hz), 200.0 (dd, CO, $^2J_{PMC}$ = 5.0, 12.0 Hz)] at 300 K has five terminal ^{13}C CO resonances, two of which are doublets of doublets due to coupling to two phosphorus nuclei. The large coupling of 68.5 Hz in **3** is retained in **5** (75 Hz) while the resonance with $^2J_{PMC}$ = 0 Hz in **3** has disappeared. These data provide conclusive proof of the stereochemical dispositions of the CO ligands inferred in this paper.

(16) $Ru_2(CO)_6[\mu\text{-}CHC(Ph)NEt_2](\mu\text{-}PPh_2)$ (**2**) and $Ru_2(CO)_6[\mu\text{-}O{=}CCHC(Ph)NEt_2](\mu\text{-}PPh_2)$ (**3**) were prepared as previously described. See: (a) Cherkas, A. A.; Mott, G. N.; Granby, R.; MacLaughlin, S. A.; Yule, J. E.; Taylor, N. J.; Carty, A. J. *Organometallics* **1988**, *7*, 1115. (b) Mott, G. N.; Granby, R.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *Organometallics* **1983**, *2*, 189.

(17) The carbon–carbon coupling constants in the above compounds are on the order of 5 Hz for cis stereochemistries and 20 Hz for trans geometries. Since the "long-range" COSY sequence with fixed delays before and after the mixing pulse compensates for low Hz/point values (when compared to the size of the coupling constant), this sequence may prove to be more routinely applicable. Bax, A.; Freeman, R. *J. Magn. Reson.* 1981, *42*, 164.

The Rate of Ring Closure of 1,1-Dimethyl-2-phenyl-1-silabuta-1,3-diene to 1,1-Dimethyl-2-phenyl-1-silacyclobutene

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Summary: Irradiation of 1,1-dimethyl-2-phenyl-1-silacyclobut-2-ene in a 3-methylpentane glass at 77 K yields 1,1-dimethyl-2-phenyl-1-silabuta-1,3-diene whose UV spectrum displays a λ_{max} at 338 nm. Flash photolysis of the silacyclobutene in a cyclohexane solution at 298 K produces the same reactive siladiene, λ_{max} which cyclizes to the starting ring structure with an activation barrier of ≈9.4 kcal/mol. Trapping studies with methoxytrimethylsilane support both the kinetic and spectral assignments.

Recent observation of transient silenes by matrix isolation spectroscopy and of stable silenes by conventional methods has revealed much of the structural and electronic details of π-bonded silicon.[1] The property that first drew

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[†] University of North Texas.

[‡] Tulane University.

(1) (a) Michl, J.; Raabe, G. *Chem. Rev.* **1985**, *85*, 419. (b) Raabe, G.; Michl, J. In *The Chemistry of Organosilicon Compounds*; Patai, S., Rappaport, Z., Eds.; Wiley: New York, in press.

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