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Fluxionality of $Fe_2(CO)_4(\eta\text{-}C_5H_5)_2$ Revisited

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Summary: The rate constant k_{13} for bridge–terminal CO exchange in the cis-bridged isomer of $Fe_2(CO)_4(Cp)_2$ (**1b**) is found by ^{13}C EXSY and DANTE studies to be close to zero at 224 and 234 K, and total band-shape simulations are also consistent with k_{13} being close to zero at higher temperatures. This result contradicts earlier dynamic ^{13}C NMR studies and implies that the Adams–Cotton pathways to direct bridge–terminal exchange in **1b** through bridge-opened rotamers have an activation barrier higher than that previously assumed.

The cyclopentadienyliron complex $Fe_2(CO)_4(\eta\text{-}C_5H_5)_2$ (1) was one of the earliest studied fluxional molecules[1,2] and is now a textbook example[3] of the dynamic behavior of metal carbonyl compounds. Numerous IR studies[4] on 1 have been reported, and the combined evidence indicates that in solution compound 1 exists as two isomeric species, trans **1a** and cis **1b**, containing bridging carbonyls, and the third unbridged isomeric form **1c**, present in ca. 1% amounts at 30 °C as estimated by Noack.[4e] Subsequent NMR studies[1,2,5-7] were consistent with this view and also showed that the isomers of 1 were in rapid exchange on the NMR time scale at ambient temperature. X-ray crystal structures of both bridged isomers **1a**[8] and **1b**[9] have been obtained.

Adams and Cotton[10,11] explained the temperature-dependent NMR behavior[1,2,5-7] of 1, in terms of a detailed mechanism (the A–C mechanism), the essential features of which are shown in Scheme I. Concerted[12] pairwise opening of the carbonyl bridges in **1a** and **1b** forms the most accessible noneclipsed rotamer of **1c**. The trans bridge-opened rotamer $\mathbf{1c}_t$ has homotopic CO ligands, and hence passage through this intermediate back to **1a** results in exchange of the bridged and terminal carbonyl environments of isomer **1a**. Bridge–terminal CO exchange in **1b** cannot occur through the cis bridge-opened intermediates $\mathbf{1c}_c$ or $\mathbf{1c}_{c*}$ *unless* there is a rotation about the Fe–Fe bond of one of the $CpFe(CO)_2$ units by $2\pi/3$ or $-4\pi/3$ (thus effecting the enantiomerization $\mathbf{1c}_c \leftrightarrow \mathbf{1c}_{c*}$). A similar rotation by $-2\pi/3$ is also the proposed route to exchange between **1a** and **1b** via $\mathbf{1c}_t$. The A–C mechanism has been used to explain the fluxional behavior of many derivatives of 1[7,13-18] and other related species.[6,19,20]

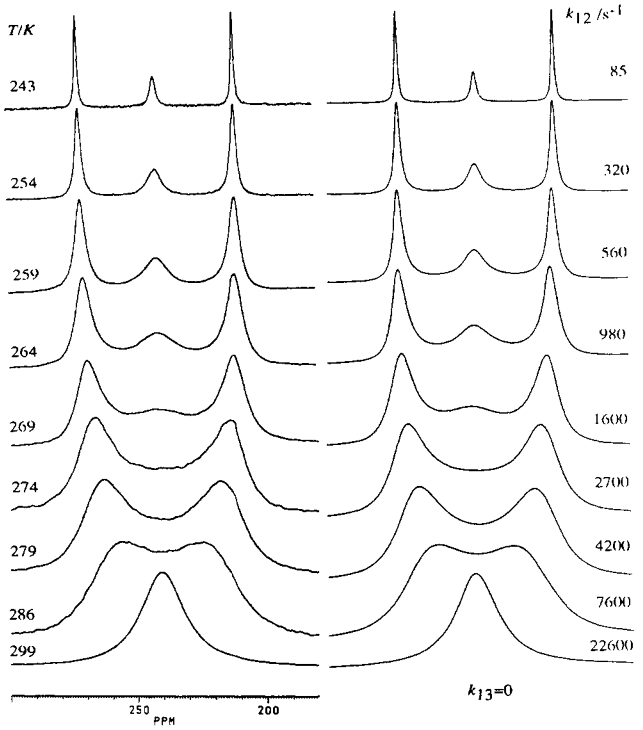
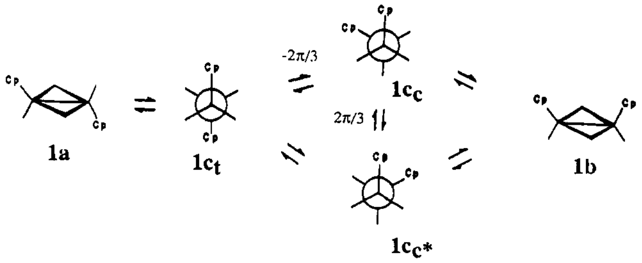


Figure 1. Experimental and simulated ^{13}C NMR spectra of 1 in the carbonyl region. The simulations were calculated with k_{13} = 0 at all temperatures.

Scheme I



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The rotations in the nonbridged isomers **1c** were assumed[10] "to be hindered by barriers of the order of magnitude of 5 kcal mol^{-1} so that they contribute significantly to the activation energy of any process in which they must occur", though it was not clear at the time which of the two A–C pathways was responsible for bridge–terminal exchange in **1b**. Two early quantitative dynamic ^{13}C NMR studies by Gansow et al.[6] and Roberts et al.[7] apparently showed that the rate constants for cis–trans isomerization and bridge–terminal CO exchange in **1b** were very similar.[21] In this study we show that there is essentially no *direct* CO exchange in the cis isomer **1b**, all exchange occurring via the trans isomer **1a**.

Results and Discussion

The ^{13}C NMR spectra of **1** shown in Figure 1 were recorded in CD_2Cl_2 on a ~35% ^{13}CO-enriched sample. Since the bridge–terminal exchange in the trans isomer **1a** is rapid at all temperatures shown, the system can be treated as a three-site exchange with the two independent rate constants k_{12} and k_{13}. The assignments are as previously given,[2,6,7] site 1 being defined here at δ 273, (bridging CO's in **1b**), site 2 at δ 242 (coalesced CO's of **1a**), and site 3 at δ 211 (terminal CO's of **1b**). Hence, the rate constant k_{12} is a measure of the cis–trans isomerization and k_{13} is the rate constant for bridge–terminal exchange in **1b**. The equilibrium constants K for cis–trans isomerization[22] obtained in CD_2Cl_2 and toluene-d_8 are given in Table S1 (supplementary material). In CD_2Cl_2 the value of K is ~2 over the temperature range 260–300 K, so that the populations of the three carbonyl sites are approximately equal. It was the appearance of the ^{13}C spectra in this temperature range (Figure 1) which alerted us to a possible discrepancy with the earlier results.[6,7] In particular, the central resonance is much broader than the other two. This behavior is not consistent with an equally populated three-site exchange having roughly equal site-to-site rate constants k_{12} and k_{13}. It is, however, consistent with a much smaller rate of bridge–terminal exchange within **1b** compared with **1a** ↔ **1b** interchange.

This suspicion was immediately confirmed by a ^{13}C EXSY spectrum measured at 224 K (Figure 2a) with the mixing time t_m = 0.02 s, which showed cross peaks between sites 1 and 2, and sites 2 and 3, *but no cross peaks* between sites 1 and 3. An EXSY spectrum at the same temperature but with t_m = 0.1 s (Figure 2b) showed weak cross peaks between sites 1 and 3. Analysis of the integrated volume intensities of the EXSY peaks by the noniterative method of Abel et al.[23] afforded the mean site-to-site rate constants k_{12} = 5.3 (±0.5) s^{-1} and k_{13} = −0.4 (±0.4) s^{-1}. Analysis of the data by the iterative method of Sales et al.[24] afforded the rate constants k_{12} = 5.4 (±0.3) s^{-1} and k_{13} = −0.2 (±0.1) s^{-1} with a goodness of fit (GOF) of 0.0018. When k_{13} was constrained to be zero, k_{12} became 5.1 (±0.2) s^{-1} with a slightly worse GOF of 0.0022. Optimizing k_{12} using small fixed values of k_{13} resulted in a progressively worse fit, and with k_{13} = 0.5 s^{-1} the GOF was substantially worse (0.0046). It should be noted that these analyses (and that for the DANTE experiment described below) do not require prior prejudice as to any relationship between the site-to-site exchange rate constants arising from mechanistic considerations. The negative value of k_{13} is taken to indicate a near-zero rate constant, and hence, the observed magnetization transfer between sites 1 and 3 seen in Figure 2b is due to second-order exchange involving the intermediacy of site 2. As expected from the well-established variation of K with solvent polarity,[4f] the rate constant k_{12} is significantly solvent-dependent. From an EXSY spectrum in toluene-d_8 at 224 K (Figure S2, supplementary material) and using the noniterative method,[23] we obtained k_{12} = 24.5 (±2) s^{-1} and k_{13} = −1.3 (±2) s^{-1}, i.e., k_{12} is some 4–5 times greater than in CD_2Cl_2 at the same temperature.

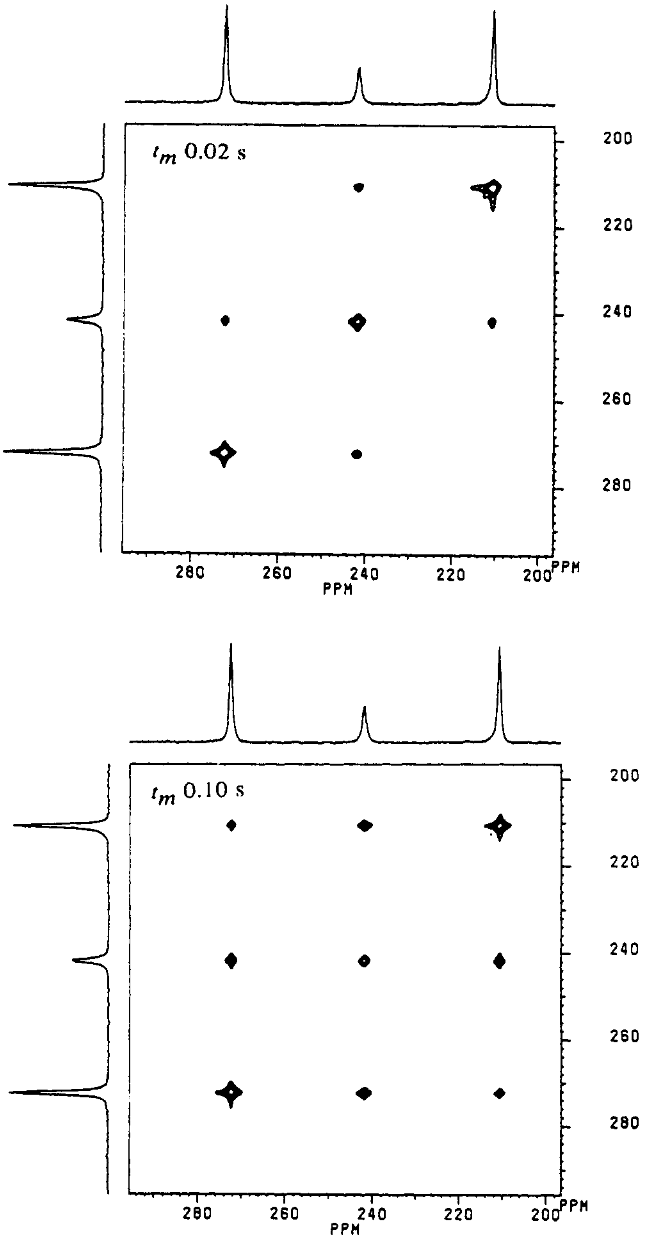

Figure 2. ^{13}C EXSY spectra of **1** (224 K, CD_2Cl_2) in the carbonyl region (a, top) with t_m = 0.02 s and (b, bottom) with t_m = 0.10 s.

We have also carried out 1D magnetization transfer experiments to further confirm these results. In separate

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[21] Gansow et al.[6] appeared to consider the processes of cis–trans isomerization and bridge–terminal CO exchange in the cis isomer **1b** as inextricably linked. The exchange matrix they used allows for population effects, but in the limit of [cis]/2 = [trans], i.e. an equally populated three-site exchange, it gives equal values for k_{12} and k_{13}. Roberts et al.[7] used the same methodology as ourselves in their band-shape analysis but found that $k_{12} \approx k_{13}$ at low temperatures. Above −17 °C they simply assumed that $k_{12} = k_{13}$, and below this temperature they made the assumption of infinitely fast bridge–terminal exchange in **1a**, which could result in some error in the calculated line widths.

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experiments, a DANTE pulse train[25] was used to obtain selective inversion of each of the sites 1–3. The evolution of nonequilibrium magnetization was analyzed as described in the Experimental Section, by using the iterative least-squares method of Grassi et al.[26] Representative plots showing the observed and calculated magnetizations at each site after inversion of resonance 2 are shown in Figure S3 (supplementary material). Using unconstrained optimization, we obtained rate constants k_{12} and k_{13} of 5.9, 0.03 s^{-1} (at 224 K) and 24.9, 0.17 s^{-1} (at 234 K). At both temperatures k_{13} is nearly zero, and when it is constrained to be zero, the least-squares error rises only insignificantly. The differences in the magnitudes of k_{13} obtained from the EXSY and DANTE experiments is a reflection of the difficulty in measuring a slow exchange process in the presence of a much faster one.

We then attempted a simulation of the total band shape in the CO region at the precoalescence and coalescence regime between 243 and 299 K, using the one unique rate constant k_{12} and with $k_{13} = 0$ at all temperatures. As can be seen from Figure 1, we were able to obtain a very satisfactory fit on the basis of these assumptions. A linear plot of ln (k/T) vs $1/T$ (Figure S4, supplementary material) results from using the rate constants calculated from the DANTE and band-shape analyses. This is strong evidence that these rate constants refer to a single exchange process. We obtain $\Delta H^* = 59.8\ (\pm 0.6)$ kJ mol^{-1} and $\Delta S^* = 39\ (\pm 2)$ J mol^{-1} K^{-1}, which compares with a value of ΔH^* of ~50 kJ mol^{-1} estimated by Cotton et al.[5] from the ^{1}H data. Of course, we are unable to eliminate a *small* contribution[27] from nonzero k_{13}. Our data are, however, entirely inconsistent with equal or nearly equal values of k_{12} and k_{13}; in particular, it was not possible to obtain a reasonable fit in the coalescence region (Figure S5, supplementary material).

In summary, our results show that the rate constant for bridge–terminal exchange within the cis isomer **1b** must be much smaller than for cis–trans isomerization and may be close to zero over the temperature range we have measured. The total CO scrambling can be rationalized by assuming only cis–trans isomerization and bridge–terminal exchange in **1a**. Obvious conclusions from our work are that (a) the *direct* A–C pathway[10,11] for bridge–terminal CO exchange in **1b**, i.e. $\mathbf{1b} \rightarrow \mathbf{1c}_c \rightarrow \mathbf{1c}_{c^*} \rightarrow \mathbf{1b}$, is of higher energy[28] than that for cis–trans interconversion, i.e. $\mathbf{1b} \rightarrow \mathbf{1c}_c \rightarrow \mathbf{1c}_t \rightarrow \mathbf{1a}$, and (b) the thermodynamic parameters reported by Gansow et al.[6] as activation parameters for bridge–terminal exchange in **1b** in reality refer to the cis–trans interconversion.

Mann and co-workers[29] have recently reported a dynamic NMR study on $Fe_2(CO)_3(CNMe)Cp_2$ which shows that the *direct* exchange between the isomers *cis*-$Fe(\mu\text{-}CO)_2(CO)(CNMe)Cp_2$ and *cis*-$Fe_2(\mu\text{-}CO)(\mu\text{-}CNMe)(CO)_2Cp_2$ is also experimentally zero. This interconversion requires a step analogous to $\mathbf{1c}_c \rightarrow \mathbf{1c}_{c^*}$; thus, our observations may be more general. It is interesting, therefore, to speculate as to why k_{13} is small. It may be, as Gansow et al.[6] and Mann et al.[29] suggest, that steric factors raise the barrier for $\mathbf{1c}_c \rightarrow \mathbf{1c}_{c^*}$.[30] Alternatively, it is possible that the cis bridge–opened rotamers $\mathbf{1c}_c/\mathbf{1c}_{c^*}$ either have a very low concentration or do not exist as *intermediates* with significant lifetimes. Some evidence, albeit circumstantial, for this suggestion comes from recent matrix isolation studies on **1** at 12 K by Rest and co-workers.[31] They find that the trans isomer **1a** undergoes photolytic bridge opening to give a species with the same IR bands as the previously observed[4c,e,f] unbridged species, while the cis isomer **1b** does not undergo photolytic bridge opening to give an all-terminal species. Since rotation about the Fe–Fe bond is unlikely at 12 K, Rest et al.[31] conclude that the IR-observed unbridged minor isomer is $\mathbf{1c}_t$. The failure of **1b** to undergo photolytic bridge cleavage may simply be due to the nonviability of $\mathbf{1c}_c$ as a stable molecule.

Experimental Section

General experimental NMR techniques and instrumentation were as previously described.[32] The equilibrium constants K for cis–trans isomerization were determined from integrations of ^{13}C NMR spectra at all temperatures where clearly resolved signals for sites 1–3 were observed. For the spectra in CD_2Cl_2, a relaxation delay of 10 s (~$20T_1$) was used to ensure that the integrations accurately reflected isomer populations, and a line-broadening factor (LB) of 50 Hz was used to increase the signal-to-noise ratio. These values were used to estimate K in the coalescence region from a plot of ln K vs $1/T$ (Figure S1, supplementary material) by assuming that ΔH was constant over the temperature range. The derived site populations were treated as variables in the band-shape analysis to obtain the best fit, using the program DNMR3,[33] though no significant deviations from those values obtained from the plot were found (Table S1). The chemical shifts of the three sites were also corrected for a small temperature dependence (ca. 1 Hz/K for resonance 1 and ca. 0.25 Hz/K for resonance 2).

The analysis of the DANTE experiments was carried out by using a program previously described by Grassi et al.[26] The data were analyzed by iteration of all variables against the nine sets of magnetization versus time curves generated from three separate experiments in which sites 1–3 were selectively inverted. For the data at 234 K, optimization with one T_1 value and with all rate constants treated as independent variables gave a least-squares error (LSE) of 0.0399, with all points fitted better than the error in integration of ±3 arbitary units. The optimized parameters are given in Table S2 (supplementary material). Setting k_{12} equal to k_{32} as required by chemical sense increased the LSE only marginally to 0.040 56, and setting k_{13} equal to zero then resulted in an insignficant rise in the LSE to 0.040 62. Setting k_{13} to small positive values above 0.3 s^{-1} raised the LSE, so that with $k_{13} = 2.0$ the error was 0.0483 with several points fitted worse than the margin of experimental error. Finally setting $k_{12} = k_{13}$ resulted in a very significantly increased LSE of 0.6932 with a large number of points being fitted worse than experimental error.

The EXSY spectra were obtained in the phase-sensitive mode, and the data were treated and analyzed using the noniterative method of Abel et al.[23] as previously described.[32] The data were also analyzed by the iterative method of Sales et al.[24] and gave essentially identical results (see text).

A sample of $Fe_2(CO)_4(Cp)_2$ obtained from commercial sources was enriched with ^{13}CO (99% ^{13}C) by stirring under 1 atm of ^{13}CO gas at 90 °C for 12 h.

Acknowledgment. Drs. B. T. Pickup and K. D. Sales are thanked for supplying programs to analyze the mul-

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[27] We find that the best fit *by eye* is with $k_{13} = 0$. With ratios of k_{13}/k_{12} at or greater than 0.04 the fit becomes substantially worse.

[28] From the maximum reasonable value of k_{13} at 234 K (~0.3 s^{-1}) we estimate that ΔG^* for bridge–terminal exchange in **1b** must be *at least* 8–10 kJ mol^{-1} greater than for cis–trans isomerization.

[29] Guillevic, M. A.; Hancox, E. L.; Mann, B. E. *J. Chem. Soc., Dalton Trans.*, in press.

[30] Steric interactions between the bulky Cp groups are greatest in the $\mathbf{1c}_c \rightarrow \mathbf{1c}_{c^*}$ route. This suggestion, however, ignores the fact that in the ground-state geometry of **1b** *the two Cp ligands are exactly eclipsed.* It may be that the pathway $\mathbf{1c}_c \rightarrow \mathbf{1c}_{c^*}$ meets a potential energy *well* in the form of **1b** rather than a *barrier*. This possibility could provide another reason for the observed near-zero rate for k_{13}, since bridge–terminal exchange is not possible in the pathway $\mathbf{1c}_c \rightarrow \mathbf{1b} \rightarrow \mathbf{1c}_{c^*}$.

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tisite magnetization transfer data and EXSY data, respectively. Dr. B. E. Mann is also thanked for a preprint of ref 29 prior to publication.

Supplementary Material Available: Tables of equilibrium constants for cis–trans isomerization and optimized parameters from magnetization transfer experiments using DANTE inversion and plot of ln K versus $1/T$ for cis–trans isomerization (Figure S1), a ^{13}C EXSY spectrum of 1 in toluene-d_8 at 224 K (Figure S2), plots of the experimental and optimized magnetization versus time curves (Figure S3), a plot of ln (k/T) versus $1/T$ for the rate constants k_{12} (Figure S4), and experimental and simulated ^{13}C NMR spectra of 1 in the carbonyl region (Figure S5) (9 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactivity of Cyclic Phosphetanes. Oligomerization, Quaternization, and Complexation with Platinum(II)

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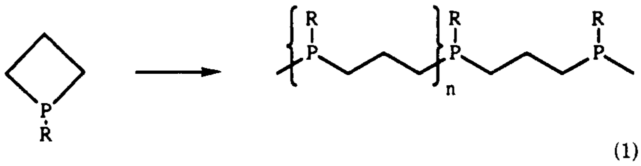
Summary: The new cyclic phosphetane *cis*- and *trans*-3-*tert*-butyl-1-phenylphosphetane (1) was prepared by a heteroatom metallacycle transfer reaction from 3-*tert*-butyltitanacyclobutane and dichlorophenylphosphine. Phosphetane 1 is stable to polymerization in the presence of electrophilic initiators in solution but forms low oligomers when the neat liquid is heated (>250 °C for 120 h). Phosphetane 1 was employed to form the phosphetane complex *cis*-dichlorobis(3-*tert*-butyl-1-phenylphosphetane)platinum(II), which was characterized by X-ray diffraction.

Polynuclear transition-metal complexes bridged by bis(diarylphosphino)- and bis(dialkylphosphino)methanes often possess novel chemical and photochemical properties.[1-4] The corresponding bis(diarylphosphino)propanes may also serve as bridging ligands to two metal centers but are sufficiently flexible to serve in some cases as chelating ligands to one metal center.[5] In the course of our recent studies of di- and trinuclear diphosphine-bridged transition-metal complexes,[1-4] we sought a general method of preparing polyphosphine ligands which were capable of supporting linear metal clusters of higher nuclearity. Polymers functionalized with phosphines are also of significant interest as catalyst supports[6-9] and in the stabilization of metal/polymer interfaces.[10] One approach to the synthesis of poly(phosphinopropanes) is the ring-opening polymerization of cyclic phosphetanes (eq 1).



(1)

Previous reports by Cremer et al. have noted the possibility of phosphetane polymerization. Upon sitting, an evacuated tube containing neat 2,2,3-trimethyl-1-phenylphosphetane was observed to become very viscous and apparently had polymerized or decomposed.[11] In addition, concentration of a highly strained tetracyclic phosphine was observed to result in polymerization.[12]

Here we describe the synthesis of the new phosphetanes *cis*- and *trans*-3-*tert*-butyl-1-phenylphosphetane (1), their reactivity toward polymerization, and their use as ligands in the preparation of the complex *cis*-dichlorobis(3-*tert*-butyl-1-phenylphosphetane)platinum(II).

Results and Discussion

Phosphetane 1 was prepared by the recently reported heteroatom metallacycle transfer reaction from 3-*tert*-butyltitanacyclobutane and dichlorophenylphosphine (eq 2).[13] Essentially equal quantities of the cis (δ −38.3 ppm) and trans (δ −6.8 ppm) isomers are evident by ^{31}P{^{1}H} NMR spectroscopy. Earlier ^{31}P{^{1}H} studies established that *cis*-phosphetanes generally exhibit chemical shifts which occur 20–30 ppm upfield of the trans isomers.[14] Similarly, the corresponding ^{1}H NMR data for *cis*- and *trans*-1 are

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

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