Two-dimensional 1H NOESY of Pd(II) .pi.-allyl complexes. The concept of reporter ligands and the molecular structure of [cyclic][Pd.eta.3-CH2CCHCH2CH2CH2)(biquinoline)]CF3SO3

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to yield complexes, all of which contain a coordinatively unsaturated square-planar Rh(I) center and coordinative saturation at the adjacent metal. It appears that these heterobimetallic complexes are best formulated as containing M→Rh dative bonds. Using the cyclopentadienyl-containing anions $[FeCp(CO)_2]^-$ and $[MoCp(CO)_3]^-$ results in only one of the dppm groups adopting a bridging configuration while the other remains chelating on Rh.

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Supplementary Material Available: Listings of additional bond lengths and angles, hydrogen atom parameters, and anisotropic thermal parameters for **5** and **6** (9 pages); listings of the observed and calculated structure factors (35 pages). Ordering information is given on any current masthead page.

Two-Dimensional ^1H NOESY of Pd(II) π-Allyl Complexes. The Concept of Reporter Ligands and the Molecular Structure of $[Pd(\eta^3\text{-}CH_2CCHCH_2CH_2CH_2)(biquinoline)]CF_3SO_3$

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A series of $[Pd(\eta^3\text{-allyl})(\text{nitrogen chelate})]CF_3SO_3$ complexes containing the coordinated β-pinene allyl or the five-membered cyclic $CH_2CCHCH_2CH_2CH_2$ allyl with biquinoline and phenanthroline (among others) as nitrogen chelate have been prepared and subjected to one- and two-dimensional ^1H NMR studies. The 2-D nuclear Overhauser effect (NOE) results with phenanthroline and bipyridyl permit the determination of subtle aspects of their three-dimensional solution structure and specifically selective distortions in the hybridization of the allyl CH_2 such that the syn proton moves slightly toward the metal and the anti proton significantly away from the palladium. Interligand NOEs may also be used to assign the coordinated face of the β-pinene allyl ligand. Not all "reporter" ligands demonstrate NOE selectivity as shown by NMR as well as the molecular structure of the cyclic allyl $[Pd(\eta^3\text{-}CH_2CCHCH_2CH_2CH_2)(biquinoline)](CF_3SO_3)$, **3a**, determined via X-ray diffraction methods. Complex **3a** crystallizes in the space group $P2_1/n$ with a = 11.062 (1) Å, b = 14.595 (3) Å, c = 14.401 (1) Å, β = 94.33 (1)°, V = 2318.6 (8) Å^3, Z = 4. Relevant bond distances are as follows: Pd–N, 2.127 (2) and 2.121 (2) Å; Pd–C(11), 2.129 (3) Å; Pd–C(12), 2.131 (2) Å; Pd–C(13), 2.168 (2) Å. The reporter protons, H(8) and H(8′), of the biquinoline are both ca. 2.5 Å from their respective π-allyl counterparts. This accounts for the substantial interligand NOEs but the lack of selectivity.

Introduction

Two-dimensional NMR methods are rapidly becoming an integral part of NMR spectroscopy[1a] and are frequently associated with the simplification and assignment problems inherent in the ^1H NMR of complicated biological molecules.[1b] Of the various possible 2-D measurements, 2-D NOESY spectroscopy is somewhat more versatile in that both structural and chemical exchange information are available,[2] often simultaneously via the use of phase-sensitive ^1H 2-D NOESY.[3] Despite this useful flexibility, this NMR form has to date found only limited application in organometallic chemistry.

π-Allyl complexes of Pd(II) are well-known[4] and recognized to be catalytic precursors in a few reactions.[5] Moreover, there is a developing interest in understanding the solution structures of chiral π-allyl intermediates as

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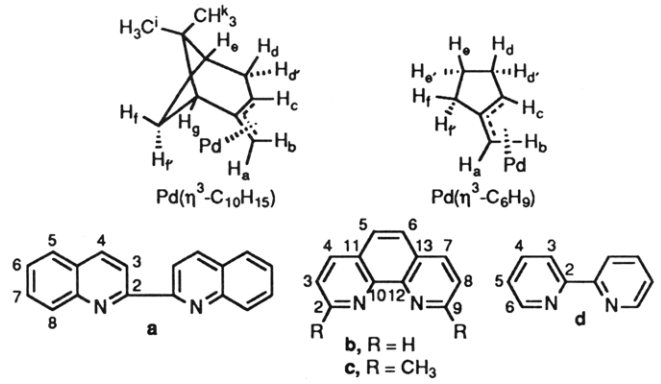
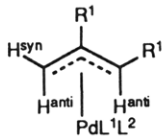
Chart I. Numbering System for the Allyl and Nitrogen Ligands in [Pd(η^3-allyl)(nitrogen chelate)]CF_3SO_3, 2 and 3[a]



[a] [Pd(η^3-$C_{10}H_{15}$)(nitrogen chelate)]CF_3SO_3 = **2**. [Pd(η^3-C_6H_9)(nitrogen chelate)]CF_3SO_3 = **3**.

these may be related to synthetic methods leading to optically active products.[6] Consequently, solution methods that afford insight into subtle structural differences and/or dynamics, e.g., 2-D ^1H NOESY, are likely to be especially welcome for this class of complex.

The ^1H NMR spectroscopy of π-allyl complexes of Pd(II) is widespread.[7-12] For complexes such as **1** it is generally



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observed[7,8,12] that the proton resonance frequency of H^{syn} is greater than that for H^{anti}. Occasionally, for R^2 substituents which bestow different "faces" upon the π-allyl ligand, e.g., for **2** in Chart I, the molecular structure in solution results from extrapolation from solid-state X-ray data.[13] Interestingly, neutron diffraction work on Ni(η^3-$C_3H_5)_2$[14] and X-ray studies of Pd–π-allyl complexes[15,16] suggest that H^{anti} is closer to the metal than H^{syn}. In view of these observations it would be useful to have a solution methodology related to the question of (i) which face of a π-allyl is coordinated, (ii) the nature of the distortion in a coordinated allyl–C(H^{anti})(H^{syn}) fragment and perhaps even (iii) whether the presumed distortion is related to the observed ^1H chemical shifts for these protons.

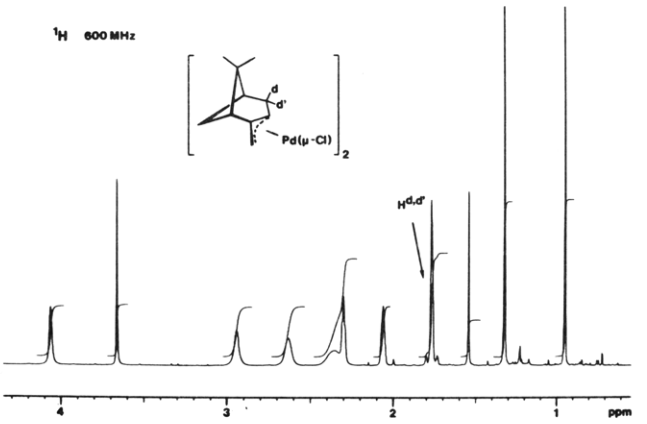

Figure 1. The 600-MHz ^1H NMR spectrum of Pd(II) Cl-bridged β-pinene allyl complex. Note that the d and d′ protons at ca. δ 1.75 form a tightly coupled AB system with almost identical chemical shifts even at this field strength ($CDCl_3$).

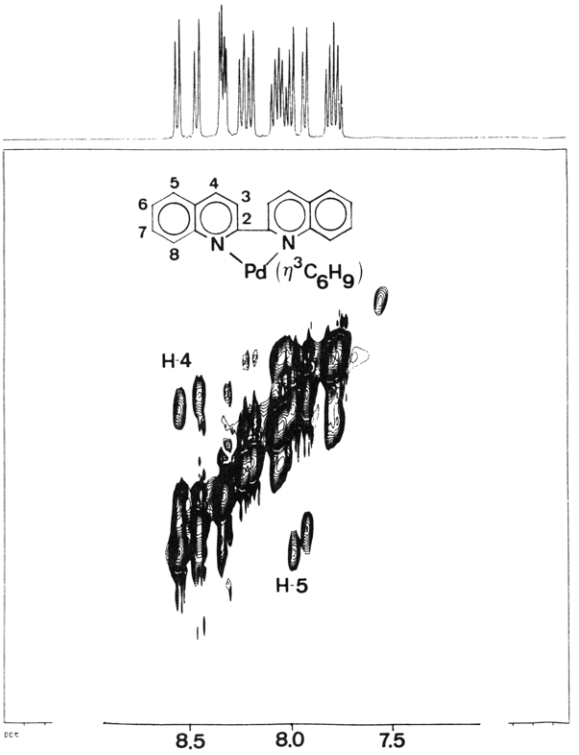

Figure 2. The 400-MHz ^1H NMR 2-D NOESY spectrum of **3a** showing only the aromatic protons. The cross peaks indicated arise from NOE from the H(4), δ ca. 8.5, and H(5), δ ca. 7.9, protons thereby connecting the spins 3 and 4 with 5–8 ($CDCl_3$).

We have approached these problems by designing and preparing complexes containing "reporter" ligands, which possess individual protons (or CH_3 groups) able to "see" across the metal (via a ^1H NOE) to the π-allyl moiety, thereby reporting on (i) which of either of the CH_2 protons is directed forward and (ii) which face of the π-allyl is coordinated (assuming of course that all the protons are assignable). Specifically our choice evolved upon chelating nitrogen ligands, e.g., as shown in **2**, since these contain protons proximate to the nitrogen which are directed toward the π-allyl moiety.

We report here on the complexes **2** and **3** with the chelating nitrogen ligands shown and demonstrate that in some cases there are selective ^1H NOEs that identify interesting molecular distortions. In support of these solution data we also present the solid-state structure of **3a**, as determined by X-ray diffraction methods.

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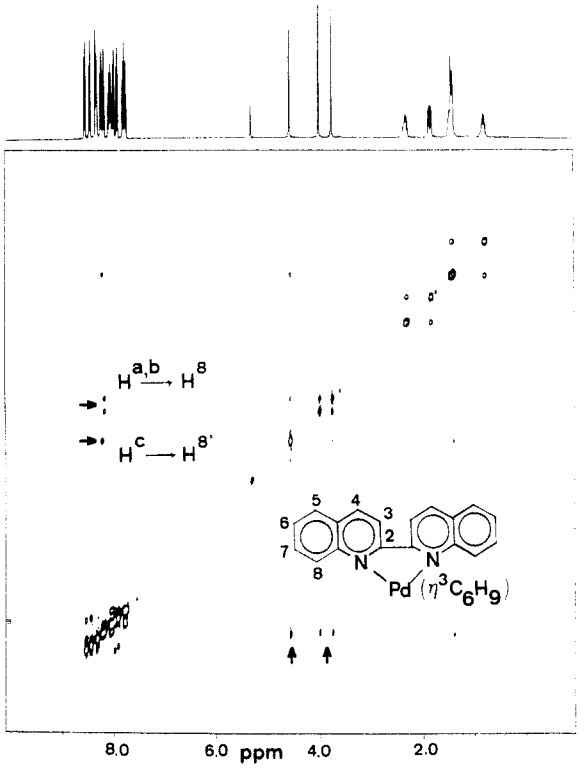

Figure 3. The 400-MHz ^{1}H NMR 2-D NOESY spectrum of **3a** showing the interligand interactions (allyl protons to H(8) and H(8′)), thereby defining the two sides of the biquinoline. Note that there is little selectivity, as H(8) sees both H^a and H^b.

Results and Discussion

Two-Dimensional Spectroscopy. For our approach to be successful it is necessary to unambiguously assign ^{1}H NMR spectra of moderately complicated Pd(II) π-allyl complexes; however, this is not always trivial even at high magnetic fields; see Figure 1. Consequently, it is useful to reiterate[7,17] the basic approach to assigning spectra: ^{13}C, ^{1}H 2-D correlations pinpoint the syn and anti protons bound to a $^{13}CH_2$ allyl moiety, since the allyl carbons are usually readily identified. In addition, NOE experiments (1- or 2-D) readily reveal two nonequivalent CH_2 allyl protons as these are close in space, whereas 2-D COSY measurements connect spins that are spin–spin coupled. The combined potential of these latter methods is nicely illustrated for the aromatic protons of the biquinoline complex **3a** in which the 12 aromatic resonances are first sorted into the spin-coupled groups H(3) plus H(4) and H(5)–H(8) and their primed counterparts via 2-D COSY and then H(4) connected to H(5) via a 2-D NOE (see Figure 2), thereby separating these 12 resonances into two groups of 6. These two groups are assigned to their positions relative to the π-allyl via the same 2-D NOESY (Figure 3) in that the reporter protons H(8) and H(8′) reveal strong cross peaks to the π-allyl protons H^a and H^b, from H(8) and H^c and $H^{d'}$ from H(8′), and this brings us to the interligand NOEs.

All of the aromatic nitrogen chelates studied to date reveal NOEs from protons oriented toward the metal to the various properly positioned allyl protons. For the 1,10-phenanthroline ligand in the β-pinene complex **2b** (Figure 4) one of the ortho protons "sees" the *syn*-allyl proton, H^a, preferentially, whereas the other ortho-chelate proton is proximate to $H^{d'}$ (identified by selective 1-D

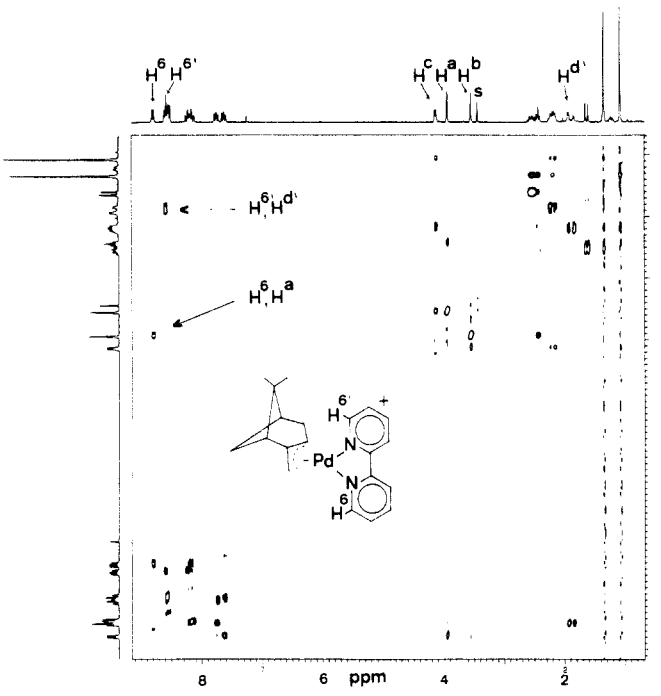

Figure 4. The 200-MHz ^{1}H NMR 2-D NOESY spectrum of **2c**. The cross peaks indicated by the arrows arise from selective interligand NOE effects, i.e., the ortho protons of the bipyridyl recognize H^a and $H^{d'}$ but *not* H^b or H^c; signal "S" = MeOH.

CH_3–H^d difference NOE experiments). This interaction with $H^{d'}$ identifies that face of the β-pinene that coordinates, i.e., the face with the CH_2 as opposed to the $C(CH_3)_2$ bridge, in keeping with expected steric considerations. The source of the preferential NOE from H(8) to H^{syn} is not immediately obvious. Taking a model based on (i) a 90° angle between the Pd, N(1), N(2) plane and the plane of the allyl carbons, (ii) the assumption that the allyl C–H bonds lie in this latter plane, and (iii) coplanarity of Pd, N(1), N(2) and the terminal allyl carbons reveals that H(8) is closer to H^{syn} than to H^{anti}, so that equal NOEs need not be observed.[18] Admittedly, this is a naive model since the majority of π-allyl X-ray structures reported reveal the allyl plane at an angle of ca. 100–110°[19] to the coordination plane such that H^{anti} would be tipped *toward* and H^{syn} *away* from the metal and remaining ligands. Nevertheless, it would be useful to estimate a "worst case" scenario, in which some or all of the preferential NOE arises due to H(8) closer to H^{syn}. Ignoring i–iii and building a model based on literature data afford H(8)–H^{syn} and H(8)–H^{anti} estimates of ca. 2.8 and 3.2 Å, respectively. Assuming the NOEs develop as a consequence of dipole–dipole relaxation, which phenomen has a $1/r^6$ distance dependence,[1] this affords an H(8)–H^{syn}/H(8)–H^{anti} NOE ratio of ca. 2.2. Conventional 1-D NOE measurements on **2d**, **3d**, and the cation $[Pd(\eta^3\text{-}CH_2C(CH_3)CH_2)(4,4'\text{-dimethylbipyridine})]^+$ reveal the following reporter proton enhancements: **2d**, 13% from H^{syn}, 4% from H^{anti}; **3d**, 15% from H^{syn}, 4% from H^{anti}; $[Pd(\eta^3\text{-}CH_2C(CH_3)CH_2)(4,4'\text{-dimethylbipyridine})]^+$, 12% from H^{syn}, 2% from H^{anti}. Obviously, the ratios of these enhancements, 3.2–6.0, are all greater than 2.2, suggesting that an additional source—we believe it to be allyl C–H twisting out of the allyl plane—is responsible for the NOE differences. Moreover, if indeed the allyl plane makes a 100° angle with the coordination plane,

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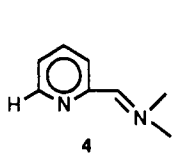
Table I. Selected ^1H NMR Data[a]

	2a[b]	2b	2c[c]	2d	3a[e]	3b	3c	3d
				π-Allyl Ligands				
H_a	3.86	4.15	4.26	3.94	4.16	4.37	4.57	4.15
H_b	3.83	3.70	3.67	3.53	3.97	3.74	3.72	3.58
H_c	4.59	4.35	4.44	4.14	4.81	4.48	4.45	4.30
H_d	1.92	2.34	2.06	2.20	1.44	2.29	1.86	2.18
$H_{d'}$	1.16	2.08	1.54	1.87	1.44	1.95	1.66	1.87
H_e	1.68	2.30	1.93	2.20	1.44	2.11	1.77	2.05
$H_{e'}$					0.80	1.68	1.20	1.64
H_f	2.02	2.62	2.22	2.50	2.34	2.80	2.55	2.72
H_f	0.79	1.77	1.00	1.60	1.86	2.47	2.14	2.44
H_g	2.02	2.55	2.22	2.42				
CH^i_3	1.03	1.41	1.07	1.32				
CH^k_3	0.94	1.16	0.96	1.05				
				Chelate Ligands				
H_2		9.17	3.15[d]			9.20	3.14[d]	
H_3	8.51	8.00	7.83	8.53	8.35	8.01	7.82	8.42
$H_{3'}$	8.65			8.51	8.33			8.42
H_4	8.48	8.77	8.50	8.20	8.47	8.75	8.47	8.24
$H_{4'}$	8.61			8.13	8.57			8.21
H_5	7.85	8.13	7.90	7.63	7.95	8.12	7.90	7.66
$H_{5'}$	7.98			7.76	8.02			7.71
H_6	7.71	8.13	7.90	8.80	7.81	8.12	7.90	8.70
$H_{6'}$	7.78			8.57	7.77			8.52
H_7	8.02	8.71	8.50		8.05	8.71	8.47	
$H_{7'}$	8.08				8.09			
H_8	8.13	8.09	7.83		8.25	8.07	7.82	
$H_{8'}$	8.29				8.20			
H_9		9.01	2.90[d]			8.93	2.95[d]	

[a] 200 MHz, $CDCl_3$, 291 K unless otherwise specified. Reporter protons for *a*, H(8); *b*, H(2), H(9); *c*, CH_3; *d*, H(6). [b] 243 K, 400.13 MHz, CD_2Cl_2. [c] 243 K. [d] CH_3 group. [e] 400.13 MHz, $CDCl_3$, 243 K.

without any CH distortions, the value of 2.2 reduces to ≤1.2, so that it is not unreasonable that the CH distortions are responsible for the majority of the selective NOE effect. The selectivity to the syn proton is consistent with either a forward twist of H^a, with H^b essentially in the π-allyl plane (or marginally away from it), or H^a in the π-allyl plane (or bent toward the metal), and H^b bent out of this plane away from the nitrogen chelate. On the basis of existing diffraction data[14-16,20] and theoretical calculations[21] combined with our structure for **3a**, we favor the latter explanation.

Interestingly, the biquinoline ligand places the protons H(8) and H(8′) so that they do indeed induce NOE in *both* the syn and anti allyl protons, although NOE to the former is sometimes more substantial. This is not unreasonable if one remembers that the reporter protons in biquinoline, shown as circles in **5**, are closer to the π-allyl than the



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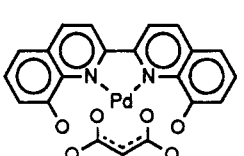

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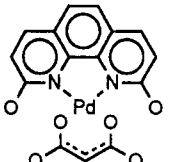

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corresponding reporter protons in a phenanthroline complex such as **6**. This implies that the choice of reporter ligand is not arbitrary: indeed, we currently recommend bipyridyl-type ligands, b or d, for a more selective interligand NOE to the π-allyl moiety. Naturally, one can imagine chelating nitrogen ligands, e.g., **4**, which select one side of a square-planar complex.[22]

It is not necessary that the π-allyl be asymmetric to observe the selectivity. Preliminary experiments[22] with a variety of η^3-$CH_2C(CH_3)CH_2$ complexes of Pd(II) gave the same result, i.e., a strong NOE to the syn proton from a suitable reporter and little or no NOE to the anti proton.

NOE results for the cyclic pentanyl complexes, **3**, are qualitatively similar in that the syn proton, H^a, experiences a strong selective NOE from bipyridyl type reporter ligands and nonselective but strong NOE with biquinoline as reporter. Not surprisingly, one of the "d" protons ($H^{d'}$ using the nomenclature of **3** in which the Pd is below the plane) is situated closer to the reporter and experiences a substantial NOE. This is useful in that it provides a starting point for a more complete assignment of the resonances H^d–H^f.

Chemical Shifts. Our knowledge of the π-allyl structural distortions in these derivatives helps us to focus on the probable source of the difference in δ ^1H between the syn and anti protons, i.e., anti to high field of syn (we show ^1H and ^{13}C data in Tables I and II). We know from theory[21] that the anti proton should be closer to the metal and this is so for $Ni(\eta^3\text{-}C_3H_5)_2$, Ni–$H^{anti}$, 2.46 (1) Å, Ni–$H^{syn}$, 2.778 (4) Å, but these distances are rather remote from the metal for a high-field shift. Moreover, NMR studies on nickel and palladium complexes[23] as well as X-ray and NMR work on an extensive set of platinum complexes[24-26] suggest that placing a proton at ca. 2.3–2.5 Å above the coordination plane usually results in deshielding; this is the opposite of what is observed for the anti proton.

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(26) Albinati, A.; Arz, C.; Pregosin, P. S. *J. Organomet. Chem.* **1988**, *356*, 367. ^1H shifts of **9a** move to lower field with increasing Pt←H—C.

Table II. Selected ^{13}C Data[a]

	2b	2c	2d	3a[c]	3b	3c	3d
				π-Allyl Ligands			
C_a	60.5	60.7	60.7	57.6	55.9	56.2	56.2
C_b[b]	145.7	143.4	145.0	129.3	124.0	128.4	126.8
C_c	69.4	68.1	68.2	82.6	79.8	79.4	79.8
C_d	30.3	31.5	29.5	25.5	32.3	34.0	33.0
C_e	40.2	39.0	39.9	33.2	25.7	25.4	26.1
C_f	34.2	35.1	33.7	34.6	35.2	34.8	35.8
C_g	47.1	45.8	46.7				
C_h	38.1	38.0	37.7				
CH^i_3	26.0	25.6	25.8				
CH^k_3	22.0	22.0	22.0				
				Chelate Ligands			
C_2	154.7	161.2	155.0	156.0	154.7	162.2	155.9
$C_{2'}$			154.6	156.2			155.0
C_3	128.2	126.0	124.0	120.2	128.2	126.6	128.4
$C_{3'}$			123.9	120.3			128.4
C_4	139.8	139.5	141.2	142.4	140.3	139.9	141.6
$C_{4'}$			140.8	142.1			141.6
C_5	126.6	126.0	127.9	129.3	126.8	126.6	124.1
$C_{5'}$			127.8	129.6			124.1
C_6	126.6	126.0	154.3	130.2	126.8	126.6	154.8
$C_{6'}$			150.3	130.2			151.6
C_7	140.2	139.8		133.5	140.1	139.7	
$C_{7'}$				133.4			
C_8	128.1	126.0		130.2	128.2	126.6	
$C_{8'}$				130.2			
C_9	150.9	161.9		145.3	151.5	161.7	
$C_{9'}$				145.3			
C_{10}	145.8	143.4		129.8	146.0	145.6	
$C_{10'}$				129.8			
C_{11}	131.0	126.0			130.9	128.1	
C_{12}	145.8	143.4			146.0	145.6	
C_{13}	131.0	126.0			130.8	128.1	
CH_3[d]		29.7				29.7	
CH_3[e]		28.7				28.9	

[a] 50.32 MHz; 296 K, unless otherwise specified; for **2a**, C_a = 62.7, C_c = 70.9. [b] Central allyl carbon. [c] 243 K, 62.87 MHz, CD_2Cl_2. [d] Opposite CH of allyl. [e] Opposite CH_2 of allyl.

Consequently, ^1H assignments based on distance to the palladium[13a,27] are questionable.

The same calculations[21] suggest that changes in hybridization affect the CH_2 of an allyl with respect to bond angles and twisting of p orbitals on carbon. Further, C–H overlap populations[14] are larger for C–H^{syn} than C–H^{anti}. Presumably as a consequence of these we find $^1J(^{13}C,H)$ values for the complexes as follows: $[Pd(\mu\text{-Cl})(\eta^3\text{-2-methallyl})]_2$, $^1J(C,H^{syn})$ = 164.0 and $^1J(C,H^{anti})$ = 158.3 Hz, and for $[Pd(\eta^3\text{-2-methylallyl})(phenanthroline)]CF_3SO_3$, $^1J(C,H^{syn})$ = 157.6 Hz, $^1J(C,H^{anti})$ = 152.6 Hz. For a variety of additional main-group and transition-metal allyl complexes similar differences in $^1J(^{13}C,H)$ are observed,[28] e.g., 161.2 and 150.8 Hz, respectively, in $Ni(\eta^3\text{-}C_3H_5)_2$ and 149.8 and 140.8 Hz, respectively, for allyllithium. Consequently bonding effects, and not separation from the metal, seem important for these chemical shifts.

In addition to these bonding differences one should not ignore anisotropic effects due to remote ligands which can cause syn and anti resonances to have *similar* positions.[12,29-31] In connection with such effects, we cannot exclude an upfield shift of the anti proton when it bends (28.9° in $Ni(\eta^3\text{-}C_3H_5)_2$[14]) out of the deshielding plane of the allyl to a more shielded region of higher electron density. It is of passing interest to consider whether various nitrogen chelate ligands markedly affect the binding of a π-allyl to Pd(II), i.e., the relative trans influence of such ligands. In Table II we show ^{13}C chemical shifts for the π-allyl carbons and suggest that, despite

Table III. Bond Lengths (Å) and Bond Angles (deg) for 3a[a]

Pd–N(1)	2.127 (2)	C(6)–C(7)	1.415 (6)
Pd–N(2)	2.121 (2)	C(6′)–C(7′)	1.425 (5)
Pd–C(11)	2.129 (3)	C(7′)–C(8)	1.379 (4)
Pd–C(12)	2.131 (2)	C(7′)–C(8′)	1.372 (4)
Pd–C(13)	2.168 (2)	C(8)–C(9)	1.406 (4)
N(1)–C(2)	1.333 (3)	C(8)–H(8)	0.94 (3)
N(1)–C(9)	1.372 (3)	C(8′)–C(9′)	1.411 (4)
N(2)–C(2′)	1.320 (3)	C(8′)–HC(8′)	0.84 (3)
N(2)–C(9′)	1.372 (3)	C(9)–C(10)	1.422 (4)
C(2)–C(2′)	1.500 (4)	C(9′)–C(10′)	1.415 (3)
C(2)–C(3)	1.400 (4)	C(11)–C(12)	1.398 (4)
C(2′)–C(3′)	1.406 (4)	C(11)–H(11)	0.95 (3)
C(3)–C(4)	1.368 (5)	C(11)–H(11′)[b]	0.70 (3)
C(3′)–C(4′)	1.362 (5)	C(12)–C(13)	1.394 (4)
C(4)–C(10)	1.392 (5)	C(12)–C(16)	1.507 (4)
C(4′)–C(10′)	1.392 (4)	C(13)–C(14)	1.506 (4)
C(5)–C(6)	1.349 (6)	C(13)–H(13)	0.83 (3)
C(5)–C(10)	1.418 (5)	C(14)–C(15)	1.541 (4)
C(5′)–C(10′)	1.435 (4)	C(15)–C(16)	1.520 (4)
C(5′)–C(6′)	1.345 (5)		
N(1)–Pd–N(2)	77.01 (8)	Pd–N(2)–C(2′)	111.1 (2)
C(11)–Pd–C(13)	68.6 (1)	Pd–N(2)–C(9′)	127.9 (2)
N(1)–Pd–C(13)	173.55 (8)	C(11)–C(12)–C(13)	120.5 (2)
N(2)–Pd–C(11)	172.7 (1)	C(11)–C(12)–C(16)	127.7 (3)
Pd–N(1)–C(2)	111.6 (2)	C(13)–C(12)–C(16)	110.2 (2)
Pd–N(1)–C(9)	128.7 (2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] H(11′) = H^{anti} in text.

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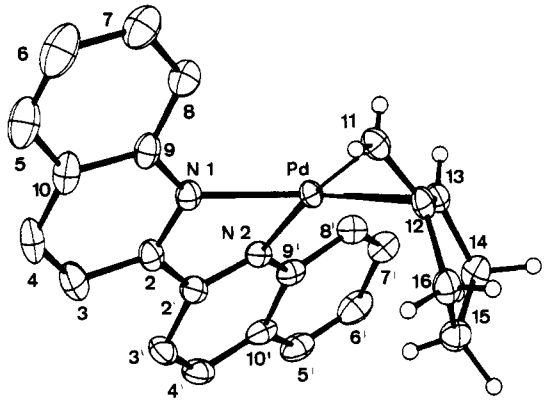

Figure 5. ORTEP view of **3a**.

differences in size, these ligands have similar donor properties.

Summarizing the solution work: ^1H 2-D NOESY is a valuable asset for determining gross and subtle structural features for allyl complexes, provided that the reporter ligand is properly chosen.

Molecular Structure of 3a. To support our solution studies, we have determined the molecular structure of **3a** via X-ray diffraction, and an ORTEP view of the molecule is shown in Figure 5. The immediate coordination sphere contains the chelate biquinoline, with essentially equivalent Pd–N separations of 2.127 (2) and 2.121 (2) Å, and the η^3-cyclopentanyl allyl shown in **3**, with the following Pd–C separations: Pd–C(11) = 2.129 (3) Å, Pd–C(12) = 2.131 (2) Å, and Pd–C(13) = 2.168 (2) Å. These latter values are in the range expected for a Pd(II) allyl with nitrogen ligands[32] in trans positions. The biquinoline has a relatively long C(2)–C(2′) separation of 1.500 (4) Å, suggesting a single bond and therefore two relatively isolated quinoline halves, in keeping with the known structures of this ligand[33] and its Ni(II)[34] and Mn(II)[35] complexes. Moreover, the alternation of bond length within the quinoline halves suggests rather localized double bonds with this effect most pronounced for the outer rings, e.g., C(5)–C(6), 1.349 (6) Å, C(5′)–C(6′), 1.345 (5) Å. The coordination angles are as expected for these ligands with N(1)–Pd–N(2) = 77° and N(1)–Pd–C(13) = 174°, and N(2)–Pd–C(11) = 173°, roughly in keeping with a distorted square-planar complex. Further, the C(12)–C(13)–C(16) plane makes an angle of 104° with the N–Pd–N plane.

Essentially all of the protons of **3a** and most importantly the protons H(8), H(8′), H(11)^{syn}, H(11)^{anti}, H(13), and H(14)^{endo} [36] have been located and refined (see the Experimental Section). The separations H(8)–H(11)^{syn}, 2.57 (4) Å, and H(8)–H(11)^{anti}, 2.49 (4) Å, are of direct relevance to our theme and clearly demonstrate the relative proximity of both the syn and anti protons to the biquinoline reporter H(8), thereby supporting the lack of NOE selectivity in this case. The pertinent separations H(8′)–H(13) and H(8′)–H(14)^{endo} are 2.47 (4) and 2.55 (4) Å, respectively. In fact these four separations are not significantly different, and this is reflected in the four strong NOE cross peaks noted in Figure 3 for this complex. It is interesting to note that the separations of the reporter carbons C(8) to the allyl protons H(11)^{syn}, 3.06 (5) Å, H(11)^{anti}, 3.29 (5) Å, and H(14)^{endo}, 2.75 (5) Å, hint at the NOE selectivity possible if the reporter ligand were not quite so close to the allyl ligand.

The torsion angles H(11)^{syn}–C(11)–C(12)–C(13) = 169.6° reveals H(11) twisted ca. 10° toward the metal and H(11)^{anti}–C(11)–C(12)–C(13) = −31.7° shows H(11)^{anti} twisted ca. 30° away from the palladium and are in good agreement with both the twist found for these protons in Ni(η^3-C_3H_5)$_2$,[14] and the discussion above on the relative NOE effects for allyl complexes with bipyridyl-type ligands. Also consistent is the 31.5° twist of H(13), the other anti proton, away from the palladium. It is interesting to note that the planes of the two biquinoline halves are 17.7° apart. Before leaving this structure we note that the anion, $CF_3SO_3^-$ is, as expected, removed from the palladium.

In summation, the structure of **3a** is as anticipated and reveals relatively short separations of ca. 2.5 Å between the protons H(8) and H(8′) and the selected cyclopentanyl protons, thereby helping us to understand the solution NOE data and the subtle structural distortions within this type of cation.

Table IV. Experimental Data for the X-ray Diffraction Study of 3

formula	$C_{25}H_{21}F_3N_2O_3PdS$
mol wt	592.93
crystal dim, mm	0.2 × 0.2 × 0.1
data coll T, °C	room temp
cryst syst	monoclinic
space group	$P2_1/n$
a, Å	11.062 (1)
b, Å	14.595 (3)
c, Å	14.401 (1)
β, deg	94.33 (1)
V, Å^3	2318.6 (8)
Z	4
ρ(calcd), g cm^{-3}	1.698
μ, cm^{-1}	9.289
radiation	Mo Kᾱ (graphite monochromated, λ = 0.71069 Å)
measd reflns	$\pm h,+k+l$
θ range, deg.	$2.2 \le \theta \le 27.0$
scan type	$\omega/2\theta$
scan width, deg	1.20 + 0.35 tan θ
max counting time, s	65
bkgd time, s	0.5 × scan time
max scan speed, deg min^{-1}	10.2
prescan rejection limit	0.55 (1.8σ)
prescan acceptance limit	0.025 (40σ)
horiz receiving slit, mm	1.90 + tan θ
vert receiving slit, mm	4.00
no. of indep data coll	5044
no of obsd reflns ($\|F_o\|^2 \ge 2.5\sigma(\|F\|^2)$)	4073
no. of params refined (n_v)	400
R^a	0.037
R_w^b	0.057
GOF^c	2.32

$^a R = \sum\|\|F_o\| - 1/k|F_c\|\|/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - 1/k|F_c|)^2/\sum w|F_o|^2]^{1/2}$, where $w = [\sigma^2(F_o)]^{-1}$ and $\sigma(F_o) = [\sigma^2(F_o^2) + f^2(F_o^4)]^{1/2}/2F_o$, with $f = 0.045$. ^{c}GOF = $[\sum w(|F_o| - (1/k)|F_c|)^2/(n_o - n_v)]^{1/2}$.

Comment

The use of a suitable reporter ligand, in our case, a phenanthroline, or bipyridyl type, affords access to selective interligand NOE data that can be used to both assign gross molecular structure and recognize subtle structural distortions. The larger biquinoline affords strong interligand NOEs but no selectivity.

Experimental Section

X-ray Measurements. Crystals suitable for X-ray diffraction of **3a** were obtained by crystallization from $CHCl_3/Et_2O$ and are

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Table V. Table of Positional Parameters, Isotopic Equivalent Thermal Factors (Å²), and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å
Pd	0.41353 (2)	0.21813 (2)	0.17925 (2)	2.458 (5)
S	0.6180 (1)	0.18250 (9)	−0.34128 (8)	4.66 (2)
F1	0.4225 (3)	0.2018 (3)	−0.4504 (3)	7.68 (8)
F2	0.3931 (3)	0.1422 (4)	−0.3194 (2)	11.7 (2)
F3	0.4670 (4)	0.0676 (3)	−0.4215 (4)	12.1 (1)
O1	0.6556 (3)	0.1177 (3)	−0.2719 (2)	6.77 (9)
O2	0.6837 (4)	0.1896 (4)	−0.4189 (3)	8.4 (1)
O3	0.0914 (6)	0.2304 (3)	0.2036 (4)	10.3 (2)
N1	0.3984 (3)	0.1529 (2)	0.0468 (2)	2.92 (5)
N2	0.4962 (2)	0.3135 (2)	0.0927 (2)	2.79 (5)
CF	0.4653 (4)	0.1531 (4)	−0.3801 (3)	5.1 (1)
C2	0.4827 (3)	0.1826 (3)	−0.0073 (2)	3.16 (7)
C2′	0.5409 (3)	0.2721 (3)	0.0214 (3)	3.17 (7)
C3	0.5099 (4)	0.1378 (3)	−0.0891 (3)	4.56 (9)
C3′	0.6299 (3)	0.3133 (3)	−0.0294 (3)	3.93 (8)
C4	0.4447 (5)	0.0615 (3)	−0.1164 (3)	5.0 (1)
C4′	0.6703 (3)	0.3992 (3)	−0.0068 (3)	4.07 (8)
C5	0.2758 (6)	−0.0445 (4)	−0.0912 (3)	6.1 (1)
C5′	0.6502 (4)	0.5392 (3)	0.0890 (3)	4.32 (8)
C6	0.1830 (6)	−0.0688 (3)	−0.0409 (4)	6.5 (1)
C6′	0.5955 (4)	0.5823 (3)	0.1569 (3)	4.85 (9)
C7	0.1592 (5)	−0.0196 (3)	0.0404 (3)	5.2 (1)
C7′	0.5020 (4)	0.5388 (3)	0.2037 (3)	4.04 (8)
C8	0.2312 (4)	0.0535 (3)	0.0701 (3)	3.92 (8)
C8′	0.4700 (3)	0.4502 (3)	0.1817 (3)	3.40 (7)
C9	0.3285 (4)	0.0790 (3)	0.0182 (2)	3.42 (7)
C9′	0.5292 (3)	0.4023 (3)	0.1131 (2)	3.05 (6)
C10′	0.6186 (3)	0.4466 (3)	0.0641 (3)	3.55 (7)
C10	0.3510 (4)	0.0312 (3)	−0.0647 (3)	4.38 (9)
C11	0.3522 (3)	0.1220 (3)	0.2765 (2)	3.45 (7)
C12	0.4453 (3)	0.1748 (3)	0.3203 (2)	3.05 (7)
C13	0.4372 (3)	0.2702 (2)	0.3205 (2)	3.01 (7)
C14	0.5564 (4)	0.3104 (3)	0.3579 (3)	3.62 (7)
C15	0.6469 (4)	0.2321 (3)	0.3446 (3)	4.05 (8)
C16	0.5727 (4)	0.1450 (3)	0.3505 (3)	3.63 (7)
HC3	0.589 (4)	0.157 (3)	−0.132 (3)	5 (1)*
HC3′	0.643 (3)	0.293 (2)	−0.072 (3)	2.9 (8)*
HC4′	0.730 (3)	0.433 (2)	−0.047 (2)	3.0 (8)*
HC4	0.461 (4)	0.032 (3)	−0.168 (3)	6 (1)*
HC5	0.303 (3)	−0.078 (3)	−0.138 (3)	4.0 (9)*
HC5′	0.718 (4)	0.567 (3)	0.047 (3)	5 (1)*
HC6	0.147 (4)	−0.111 (3)	−0.060 (3)	5 (1)*
HC6′	0.607 (6)	0.659 (5)	0.181 (5)	12 (2)*
HC7′	0.458 (3)	0.568 (3)	0.243 (3)	4.0 (9)*
HC7	0.087 (5)	−0.036 (4)	0.072 (4)	8 (1)*
HC8	0.215 (3)	0.091 (2)	0.121 (2)	2.5 (7)*
HC8′	0.422 (3)	0.417 (3)	0.210 (3)	3.6 (8)*
H11	0.360 (3)	0.058 (3)	0.266 (3)	3.4 (8)*
H11′	0.295 (4)	0.142 (3)	0.278 (3)	5 (1)*
H13	0.371 (4)	0.297 (3)	0.320 (3)	3.7 (9)*
H14	0.586 (3)	0.354 (3)	0.327 (2)	3.7 (9)*
H14′	0.556 (3)	0.328 (3)	0.425 (2)	2.9 (7)*
H15′	0.665 (3)	0.232 (3)	0.290 (3)	3.0 (8)*
H15	0.729 (5)	0.251 (4)	0.386 (4)	6 (1)*
H16	0.582 (4)	0.128 (3)	0.406 (3)	4.5 (9)*
H16′	0.600 (3)	0.090 (3)	0.314 (2)	2.5 (7)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^1/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ac(\cos\beta)B(1,3)]$.

air stable. A regular prismatic crystal was mounted in a random orientation on a Nonius CAD4 diffractometer for space group determination and data collection. Cell constants were obtained by a least-squares fit of the 2θ values of 25 high-angle ($10.0 < 2\theta < 17.0$) reflections using the standard CAD4 programs. Crystallographic and data collection parameters are listed in Table IV.

Data were collected at variable scan speed to obtain constant statistical precision on the recorded intensities. Three standard reflections were measured every hour to monitor the stability of the crystal, while the orientation was checked every 300 reflections by measuring three standards. No significant variations were detected. Data were corrected for Lorentz and polarization factors,[37] and an empirical absorption correction was applied with

Table VI. Yields and Microanalytical Data

	yield, %	anal. calcd (found) C	H	N
2a	88	53.83 (53.20)	4.21 (4.58)	4.33 (4.27)
2b	92	48.39 (48.33)	4.06 (4.20)	4.91 (5.19)
2c	88	50.13 (50.02)	4.54 (4.83)	4.68 (4.76)
2d	92	46.12 (46.54)	4.24 (4.28)	5.12 (4.95)
3a	76	50.64 (50.66)	3.57 (3.68)	4.72 (4.90)
3b	82	44.16 (44.09)	3.32 (3.37)	5.42 (5.54)
3c	89	46.29 (45.76)	3.88 (3.76)	5.14 (5.26)
3d	89	41.43 (41.27)	3.48 (3.43)	5.68 (5.84)

azimuthal (Ψ) scans of six reflections at high χ angles ($86.9 \leq \chi \leq 89.1$) using the SDP programs;[38] transmission factors were in the range 0.953–1.000. The standard deviations on intensities were calculated in terms of statistics alone. An $F_o = 0.0$ was given to those reflections having negative net intensities. The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least-squares methods, minimizing the function $\sum w(|F_o| - 1/k|F_c|)^2$, where k is the usual scale factor (see Table IV).

Anisotropic temperature factors were used for all non-hydrogen atoms. The chemically significant hydrogen atoms H(8), H(8′), H(11), and H(11′) were located on a Fourier difference map while the coordination of the remaining hydrogens was calculated assuming standard geometries (C–H = 0.95 Å). All hydrogens were then refined in the final least-squares cycles. Upon convergence (no parameter shift $>0.1\sigma(p)$) the final Fourier difference map showed no significant feature.

Scattering factors were taken from the literature,[39] and the contribution of the real and imaginary part of the anomalous dispersion was taken into account.[39] No extinction correction was deemed necessary. All calculations were carried out using the SDP crystallographic package.[38]

Final coordinates and equivalent temperature factors are given in Table V.

Preparative Section. $[Pd(\mu\text{-}Cl)(\eta^3\text{-allyl})]_2$ complexes were prepared by using literature methods.[40,41]

Synthesis of 3a. Complex $[Pd(\mu\text{-}Cl)(CH_2CCHCH_2CH_2CH_2)]_2$ (50.4 mg, 0.11 mmol) in 4 mL of methanol was treated with solid 2,2′-biquinoline (57.9 mg, 0.22 mmol), and the resulting solution stirred for ca. 15 min to afford a clear pale yellow solution. Addition of $Tl(CF_3SO_3)$ (79.8 mg, 0.22 mmol) affords immediate precipitation of TlCl. Continued stirring for 10 min was followed by filtration through Celite and removal of the solvent in vacuo. The resulting solid was recrystallized from $CHCl_3/Et_2O$ and dried under vacuum, 102 mg (76%). **3b–d** were prepared analogously.

Synthesis of 2b. The β-pinene allyl complex in Figure 1 (39.7 mg, 0.07 mmol) in 4 mL of methanol was treated with solid 1,10-phenanthroline (28.4 mg, 0.14 mmol), and the resulting solution stirred for 15 min. Addition of $Tl(CF_3SO_3)$ (50.6 mg, 0.14 mmol) affords immediate precipitation of TlCl. Continued stirring for 5 min was followed by filtration through Celite and removal of the solvent in vacuo. The yellow crude product so obtained, 73.2 mg (92%), was dried under vacuum and used directly. The remaining three complexes were prepared analogously. Yields and microanalyses for the eight complexes are given in Table VI.

One- and two-dimensional NMR spectra were measured by using Bruker WM-250 and AM-200 NMR spectrometers. Standard NOESY pulse sequences were applied[1] using mixing times of 1-2 s to develop the appropriate Overhauser effects. There are differences to be expected between 1- and 2-D NOEs, and specifically we estimate that cross peaks representing significantly less than 5% enhancements will be difficult to detect.[42] All

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samples were degassed by the freeze–thaw method and then sealed.

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Supplementary Material Available: Tables of bond distances, bond angles, and thermal parameters (4 pages); a listing of F_o and F_c (42 pages). Ordering information is given on any current masthead page.

Photoinduced Hydrometalation and Hydrogenation of Activated Olefins with Molybdenum and Tungsten Dihydrides (Cp_2MH_2)

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The early-transition-metal hydrides Cp_2MoH_2, Cp_2WH_2, and Cp_2ReH rapidly form a series of electron donor–acceptor (EDA) complexes with various activated olefins as shown by the spontaneous appearance of vivid colors, the absorption energies of which correlate with the electron affinity of the olefinic acceptor and the oxidation (ionization) potential of the hydridometal donor in accord with Mulliken theory. Deliberate excitation of the charge-transfer absorption band leads to the quantitative hydrometalation of fumaronitrile by Cp_2MoH_2 at 25 °C, and the structure of the σ hydrido alkyl adduct $Cp_2Mo(CHCNCH_2CN)H$ (I) has been established by X-ray crystallography. (space group $P2_1$, monoclinic, with a = 8.090 (3) Å, b = 10.282 (4) Å, c = 8.316 (3) Å, β = 116.92 (3)°, V = 617 Å^3, Z = 2, R = 0.028, R_w = 0.028 for 1802 reflections with $I > 3\sigma$ having $2\theta \leq 60°$). Under the same photochemical conditions, the tungsten analogue Cp_2WH_2 effects quantitative hydrogenation and leads to succinonitrile together with the olefinic π-adducts to tungstenocene in high yields. (In both cases, the thermal (dark) processes are nonexistent.) The charge-transfer mechanism for olefin hydrometalation and hydrogenation stemming from charge separation in the EDA complex (i.e. $[Cp_2MH_2^{\bullet+},{>}C^{-}–C^{\bullet}{<}]$) is delineated in terms of the one-electron-oxidation potential E°_{ox} of the hydridometal species and the subsequent facile proton transfer from the labile cation radical $Cp_2MH_2^{\bullet+}$ (M = Mo, W) to the acceptor moiety. The close similarity of the photoinduced process for olefin hydrometalation and hydrogenation of various activated olefins with those effected thermally at higher temperatures is discussed.

Introduction

Metal catalysis of olefin and arene hydrogenation is critically dependent on hydridometal (HM) intermediates.[1] Indeed, the separate isolation of various hydridometal complexes and their direct addition to unsaturated centers represent a viable procedure for the preparation of different types of hydrocarbyl derivatives.[2-6] The mechanism of the activation process leading to reactive intermediates in such hydrometalations is less clear. Thus, the relevance of intermediate free radicals was initially suggested on the basis of stereochemistry and relative reactivities[7] and later confirmed by EPR studies.[8] Observation of CIDNP has led to radical-pair mechanisms that stem from an overall hydrogen atom transfer to olefinic substrates.[9-11] Although the prior ligation of substrate to HM has been established in some cases,[12] it is noteworthy that CIDNP has so far been reported only in those systems for which there is no evidence of precoordination. In the latter case, the mechanistic basis for the intermolecular interactions leading to hydrogen atom transfer from the hydridometal intermediate to the substrate is lacking. Thus, the report of transient charge-transfer (CT) absorption bands during hydrometalations with tungsten and molybdenum hydrides is particularly interesting.[13] Since such absorption bands are diagnostic of electron donor–acceptor (EDA) precursor complexes, as in eq 1 (Scheme I),[14,15] the charge-transfer

Scheme I

$$HM + {>}C{=}C{<} \rightleftharpoons [HM,{>}C{=}C{<}] \quad (1)$$

$$[HM,{>}C{=}C{<}] \rightarrow [HM^{\bullet+},{>}C^{-}{-}C^{\bullet}{<}] \text{ etc.} \quad (2)$$

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