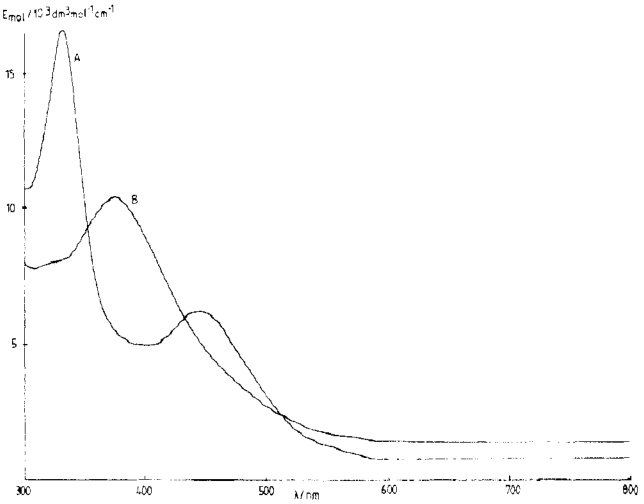

Figure 3. UV–Visible spectra of [Pd{o-$C_6H_4(TeMe)_2$}I_2] (A) and [{Pd(o-C_6H_4(TeMe)Te)I}$_4$] (B) in DMSO solution.

shifts in ortho-substituted telluroethers o-C_6H_4(TeMe)(R) (R = H, OMe, NMe_2, Cl, PMe_2, etc.)[25,26] lie in the range 200–375 ppm, and thus the resonance of the TeMe group in free o-C_6H_4(TeMe)Te^- is expected to lie in (or near) this range. Bildstein et al.[27] have reported ^{125}Te chemical shifts for a variety of telluride anions in $Li^+[o\text{-}C_6H_4Te(R)]^-$ which lie to low frequency of those of $TeMe_2$ (−229 to −13 ppm). From comparisons of the chemical shifts in the pairs o-C_6H_4(OMe)(TeMe)/o-C_6H_4(OMe)Te^- (+206/−229 ppm), o-C_6H_4(NMe_2)(TeMe)/o-C_6H_4(NMe_2)Te^- (+236/−211 ppm), and PhTeMe/PhTe^- (+329/−122 ppm), it appears that the chemical shifts of the tellurides lie approximately 450 ppm to low frequency from those of the corresponding telluroethers. Hence, from o-$C_6H_4(TeMe)_2$ (δ = 372)[26] we can estimate the shift of the telluride group in o-C_6H_4(TeMe)Te^- as −80 ± 50 ppm. When the ligand is coordinated to a metal, a large high-frequency shift is expected, due both to electron donation to the metal and to the presence of a five-membered chelate ring.[13] The presence of only one resonance for Te(Me) and one for Te^- in the tetramer (and of the single ^{1}H NMR TeMe resonance), indicate that only one environment is present for each, whereas several stereoisomers are possible. This could be due to fast inversion on the NMR time scale or to the presence of only one isomer in significant amounts. Unfortunately the very poor solubility prevents a variable-temperature NMR study to investigate this matter further (even at ambient temperature the ^{125}Te data required ca. 400 000 transients for an adequate signal to noise ratio to be achieved).

Attempts to realkylate the title complex by treatment with excess MeI in CH_2Cl_2 or ethanol were unsuccessful.

Acknowledgment. We thank the Science and Engineering Research Council for financial support (T.K. and M.D.S.) and Professor M. B. Hursthouse and the SERC for the X-ray data collection.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atomic coordinates, and full bond length and bond angle data (4 pages); a listing of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Reactivity of the Chiral Rhenium Phenyl Complex (η^5-C_5H_5)Re(NO)(PPh_3)(C_6H_5)

Sénamé K. Agbossou, Gerardo S. Bodner, Alan T. Patton, and J. A. Gladysz*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received August 15, 1989

Reaction of (η^5-C_5H_5)Re(NO)(PPh_3)(Cl) and C_6H_5Cu gives chiral, racemic phenyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(C_6H_5) (**1**, 82–92%), which undergoes a spontaneous resolution when crystallized from CH_2Cl_2/hexanes. The crystal structure (monoclinic, $P2_1$, a = 9.261 (2) Å, b = 14.142 (3) Å, c = 10.722 (2) Å, β = 112.74 (1)°, Z = 2) exhibits an unexpected Re–C_α conformation that places one ortho carbon in the region between the nitrosyl and PPh_3 ligands. Reaction of **1** and $HBF_4 \cdot O(C_2H_5)_2$ in CH_2Cl_2 at −80 °C gives, as the first species detected by NMR, η^2-benzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}C_6H_6)]^+BF_4^-$ (**2**). Between −70 and −40 °C, **2** converts to dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ (**3**), even in the presence of excess benzene. Reaction of **1** and $Ph_3C^+PF_6^-$ in CH_2Cl_2 at −80 °C gives bis(vinyl)alkylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)({=}CH{-}CH{=}CH{-}CH(CPh_3){-}CH{=}CH)]^+PF_6^-$ (**7**), which decomposes above −40 °C to **3** and other products that ultimately yield tetraphenylmethane.

Introduction

We have had an ongoing interest in the synthesis, structure, and reactivity of complexes of the chiral, electron-rich rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ and unsaturated hydrocarbon fragments such as vinyls (—CH=CHR),[1] allyls (—CH_2CH=CHR),[2] alkylidenes (=CHR),[3] and alkenes (H_2C=CHR).[4] Many of these complexes undergo highly stereoselective reactions with

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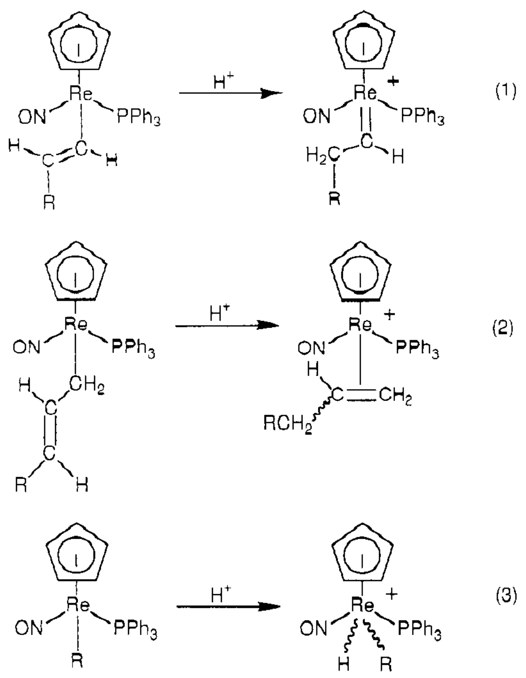
Scheme I. Representative Reactions of Rhenium Hydrocarbyl Complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C_xH_y)$ with Strong Acids

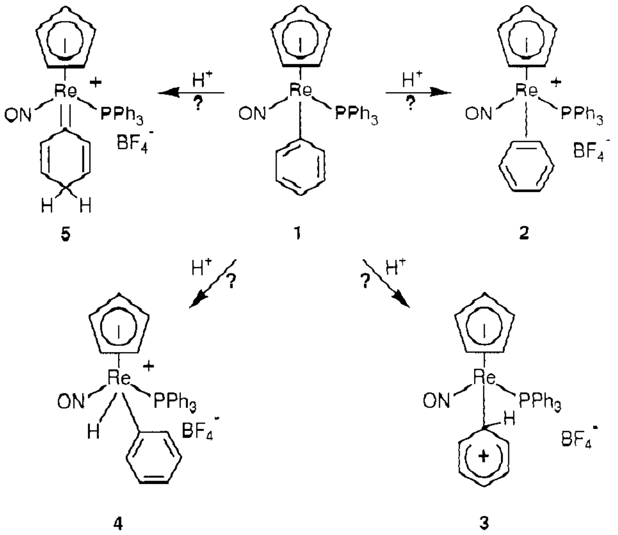


electrophiles or nucleophiles that lead to new ligand-based chiral centers. We desired to extend these studies to new classes of compounds and accordingly set out to access σ-aryl complexes of the general formula $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Ar)$.

In particular, we sought to define the reactivity modes that might be exhibited by such aryl complexes toward electrophiles. For example, previous work has shown that vinyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}CHR)$ and strong acids react to give cationic alkylidene complexes as depicted in Scheme I, eq 1.[1] Allyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH{=}CHR)$ and strong acids react to give cationic alkene complexes as shown in Scheme I, eq 2.[2] Saturated alkyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(R)$ and $HBF_4{\cdot}O(C_2H_5)_2$ react to give labile cationic alkyl hydride complexes, as shown in Scheme I, eq 3.[5] When eqs 1 and 2 are monitored by NMR at −78 °C, no evidence is found for a cationic alkyl hydride intermediate analogous to the product of eq 3.

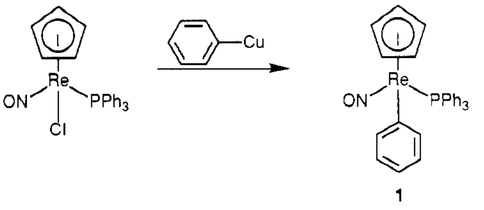
In principal, the target aryl complexes and strong acids could react to give any of the types of products shown in Scheme I and others as well. Some possibilities are sketched in Scheme II. Significantly, several of these species are of independent interest in connection with arene carbon–hydrogen bond activation mechanisms.[6,7] In this paper, we describe (1) a high-yield synthesis of phenyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C_6H_5)$ (1), (2) the crystal structure of 1, which reveals a spontaneous kinetic resolution and some unexpected conformational features, and (3) reactions of 1 and electrophiles that lead to both η^2-benzene[6–10] and alkylidene complexes.

Scheme II. Some Possible Reactions of Phenyl Complex 1 with $HBF_4\bullet O(C_2H_5)_2$ ("H^+")



Results

1. Synthesis and Structure of Phenyl Complex 1. Graham has previously shown that the *carbonyl*-substituted chloride complex $(\eta^5\text{-}C_5H_5)Re(NO)(CO)(Cl)$ and arylcopper reagents ArCu react to give aryl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(CO)(Ar)$.[11] Hence, phenylcopper was generated from $CuBr{\cdot}S(CH_3)_2$ and C_6H_5MgBr[12] and added to *phosphine*-substituted chloride complex[13] $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Cl)$ (eq 4). Workup gave chiral, racemic phenyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C_6H_5)$ (1) in 82–92% yields as an air-stable, spectroscopically pure orange powder. Crystallization from CH_2Cl_2/hexanes gave analytically pure red-orange prisms.



(4)

Complex 1 was characterized by NMR (^1H, ^{13}C, ^{31}P), IR, and mass spectroscopy (Experimental Section). The cyclopentadienyl proton ^1H NMR chemical shift (δ 5.15) was slightly downfield of those of analogous vinyl (δ 5.08–4.92),[1] allyl (δ 4.96–4.86),[2] and alkyl (δ 4.92–4.89)[3] complexes. The phenyl ligand exhibited resolved ortho, meta, and para ^1H NMR resonances that were separated from the PPh_3 proton resonances. These were slightly broadened in spectra recorded at −90 °C, but no decoalescence was observed. The ^{13}C NMR spectrum similarly showed distinct

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Table I. Summary of Crystallographic Data for $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C_6H_5)$ (1)

mol formula	$C_{29}H_{25}NOPRe$
formula weight	620.7
cryst syst	monoclinic
space group	$P2_1$
cell dimens	
a, Å	9.2614 (16)
b, Å	14.1424 (31)
c, Å	10.7222 (21)
β, deg	112.743 (14)
V, Å^3	1216.7 (4)
Z	2
d_{calcd}, g/cm^3 (16 °C)	1.58
d_{obs}, g/cm^3 (22 °C)	1.59
cryst dimens, mm	0.37 × 0.20 × 0.11
radiation, Å	λ(Mo Kα) 0.71069
data coll method	θ–2θ
scan speed, deg/min	2.0
reflns measd	$3.0° < 2\theta < 50°$; $h,\pm k,\pm l$
scan range	Kα_1 −1.3 to Kα_2 +1.3
no. of reflns between stds	97
total unique data	5729
obsd data, $I > 3\sigma(I)$	5098
abs coeff (μ), cm^{-1}	40.96
min abs corr	0.071
max abs corr	0.227
no. of variables	298
$R = \sum(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\sum\lvert F_o\rvert$	0.028
$R_w = \sum(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)w^{1/2}/\sum\lvert F_o\rvert w^{1/2}$	0.35
goodness of fit	1.36

Table II. Atomic Coordinates of Non-Hydrogen Atoms in 1

atom	x	y	z
Re	−0.471 32 (2)	0.000 00 (0)	−0.396 19 (2)
P	−0.455 35 (14)	0.090 68 (9)	−0.195 10 (13)
N	−0.616 79 (55)	0.071 84 (35)	−0.522 55 (50)
O	−0.707 04 (66)	0.119 81 (38)	−0.613 24 (51)
C1	−0.631 80 (64)	−0.095 03(40)	−0.359 66 (55)
C2	−0.591 55 (74)	−0.188 42 (43)	−0.304 61 (64)
C3	−0.701 63 (88)	−0.254 13 (45)	−0.301 62 (67)
C4	−0.858 37 (89)	−0.228 94 (53)	−0.345 79 (71)
C5	−0.902 04 (73)	−0.138 86 (50)	−0.393 85 (65)
C6	−0.791 14 (66)	−0.073 09 (42)	−0.402 49 (60)
C11	−0.201 23 (61)	−0.005 70 (82)	−0.312 04 (66)
C12	−0.257 02 (93)	0.016 40 (77)	−0.459 68 (95)
C13	−0.348 30 (91)	−0.057 99 (69)	−0.538 94 (85)
C14	−0.347 56 (81)	−0.129 11 (57)	−0.439 71 (94)
C15	−0.256 22 (75)	−0.095 34 (52)	−0.298 36 (78)
C21	−0.633 74 (55)	0.118 68 (33)	−0.163 05 (54)
C22	−0.762 22 (64)	0.154 83 (37)	−0.276 18 (62)
C23	−0.894 65 (67)	0.184 03 (43)	−0.256 12 (71)
C24	−0.899 87 (74)	0.177 93 (43)	−0.121 21 (81)
C25	−0.773 73 (93)	0.142 03 (52)	−0.006 20 (85)
C26	−0.642 12 (67)	0.110 54 (39)	−0.028 71 (61)
C31	−0.373 02 (55)	0.210 15 (37)	−0.184 23 (52)
C32	−0.324 58 (68)	0.243 34 (41)	−0.290 73 (60)
C33	−0.257 01 (77)	0.333 38 (47)	−0.277 12 (77)
C34	−0.233 45 (82)	0.338 14 (45)	−0.156 15 (84)
C35	−0.281 92 (97)	0.355 55 (52)	−0.052 00 (91)
C36	−0.353 84 (75)	0.267 11 (40)	−0.065 09 (66)
C41	−0.325 92 (59)	0.034 64 (35)	−0.026 60 (55)
C42	−0.183 61 (64)	0.072 65 (40)	0.063 12 (60)
C43	−0.090 86 (68)	0.023 55 (45)	0.188 40 (65)
C44	−0.140 92 (84)	−0.063 12 (52)	0.221 58 (70)
C45	−0.280 92 (78)	−0.100 05 (45)	0.130 59 (67)
C46	−0.375 66 (72)	−0.052 00 (40)	0.006 88 (62)

ipso, ortho, meta, and para phenyl ligand resonances (143.0, 142.4, 126.3, 120.5 ppm) that correlated closely with those of related iron complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2(C_6H_5)$ (145.4, 145.0, 127.5, 122.8 ppm) and $(\eta^5\text{-}C_5H_5)Fe(CO)(P(OPh)_3)(C_6H_5)$ (150.0, 146.5, 126.4, 121.7 ppm).[14]

Table III. Bond Lengths in 1 (Å)

Re–P	2.353 (1)	Re–N	1.772 (5)
N–O	1.184 (7)	Re–C1	2.139 (6)
Re–C11	2.311 (5)	Re–C12	2.320 (6)
Re–C13	2.303 (7)	Re–C14	2.287 (7)
Re–C15	2.289 (7)	P–C21	1.845 (5)
P–C31	1.839 (5)	P–C41	1.836 (5)
C1–C2	1.425 (8)	C2–C3	1.388 (9)
C3–C4	1.390 (11)	C4–C5	1.367 (10)
C5–C6	1.413 (8)	C6–C1	1.403 (8)
C11–C12	1.408 (11)	C11–C15	1.393 (13)
C12–C13	1.392 (13)	C13–C14	1.416 (12)
C14–C15	1.428 (10)	C21–C22	1.388 (7)
C21–C26	1.390 (7)	C22–C23	1.381 (8)
C23–C24	1.381 (10)	C24–C25	1.385 (10)
C25–C26	1.396 (9)	C31–C32	1.394 (7)
C31–C36	1.398 (8)	C32–C33	1.402 (9)
C33–C34	1.388 (11)	C34–C35	1.371 (11)
C35–C36	1.399 (9)	C41–C42	1.386 (7)
C41–C46	1.395 (7)	C42–C43	1.405 (8)
C43–C44	1.396 (10)	C44–C45	1.369 (10)
C45–C46	1.392 (8)		

Table IV. Bond Angles in 1 (deg)

N–Re–P	94.8 (2)	P–C41–C42	123.5 (1)
N–Re–C1	95.6 (2)	P–C41–C46	116.3 (4)
P–Re–C1	90.6 (1)	C21–P–C31	99.0 (2)
Re–N–O	174.9 (5)	C31–P–C41	103.5 (2)
Re–C1–C6	121.8 (4)	C41–P–C21	103.9 (2)
Re–C1–C2	123.7 (4)	C21–C22–C23	121.2 (5)
C1–C2–C3	123.0 (6)	C22–C23–C24	119.8 (6)
C2–C3–C4	120.4 (6)	C23–C24–C25	120.4 (6)
C3–C4–C5	118.8 (6)	C24–C25–C26	119.2 (6)
C4–C5–C6	120.8 (6)	C25–C26–C21	120.8 (6)
C5–C6–C1	122.6 (6)	C26–C21–C22	118.5 (5)
C6–C1–C2	114.2 (5)	C31–C32–C33	119.6 (6)
C11–C12–C13	109.4 (9)	C32–C33–C34	122.0 (4)
C12–C13–C14	107.2 (7)	C33–C34–C35	119.8 (6)
C13–C14–C15	107.8 (7)	C34–C35–C36	120.9 (7)
C14–C15–C11	107.7 (7)	C35–C36–C31	119.6 (6)
C15–C11–C12	107.9 (7)	C36–C31–C32	119.6 (5)
Re–P–C21	120.3 (2)	C41–C42–C43	119.4 (5)
Re–P–C31	116.0 (2)	C42–C43–C44	120.3 (6)
Re–P–C41	111.2 (2)	C43–C44–C45	119.4 (6)
P–C21–C22	118.5 (4)	C44–C45–C46	121.3 (6)
P–C21–C26	122.9 (4)	C45–C46–C41	119.5 (6)
P–C31–C32	120.8 (4)	C46–C41–C42	120.2 (5)
P–C31–C36	119.5 (4)		

Next, X-ray data were collected on 1 as outlined in Table I. Refinement, described in the Experimental Section, indicated a polar space group with only one enantiomer of 1 in the unit cell. Presumably equal amounts of both enantiomers of racemic 1 crystallized, but in separate crystals. A second batch of 1 was crystallized, and X-ray data indicated an identical unit cell and space group. Hence, the spontaneous resolution is reproducible.

The structures depicted in Figure 1 are enantiomeric to those found in the arbitrary crystal of 1 refined. This reversal of configuration facilitates comparisons with previously published ORTEP diagrams of related compounds.[1-4] Atomic coordinates, bond lengths, and bond angles are listed in Tables II–IV. Tables of anisotropic thermal parameters and calculated and observed structure factors are given in the supplementary material (see the paragraph at the end of the paper). The distance between the ortho-hydrogen atom on C2 of the phenyl ligand and the cyclopentadienyl hydrogen atom on C14 was found to be 2.89 Å. The corresponding distance to C14 was 3.23 Å.

We sought to further define the structural features of the phenyl ligand. First, the least-squares phenyl ligand plane was calculated. Carbon atoms C1–C6 showed only small deviations from the plane (0.014 to −0.023 Å). The rhenium was somewhat removed from the plane (0.27 Å), and the Re–C1 (Re–C_α) bond made a 6.9° angle with the

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[14] (a) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981; p 108. (b) See also: Hunter, A. D.; Szigety, A. B. *Organometallics* **1989**, *8*, 2670.

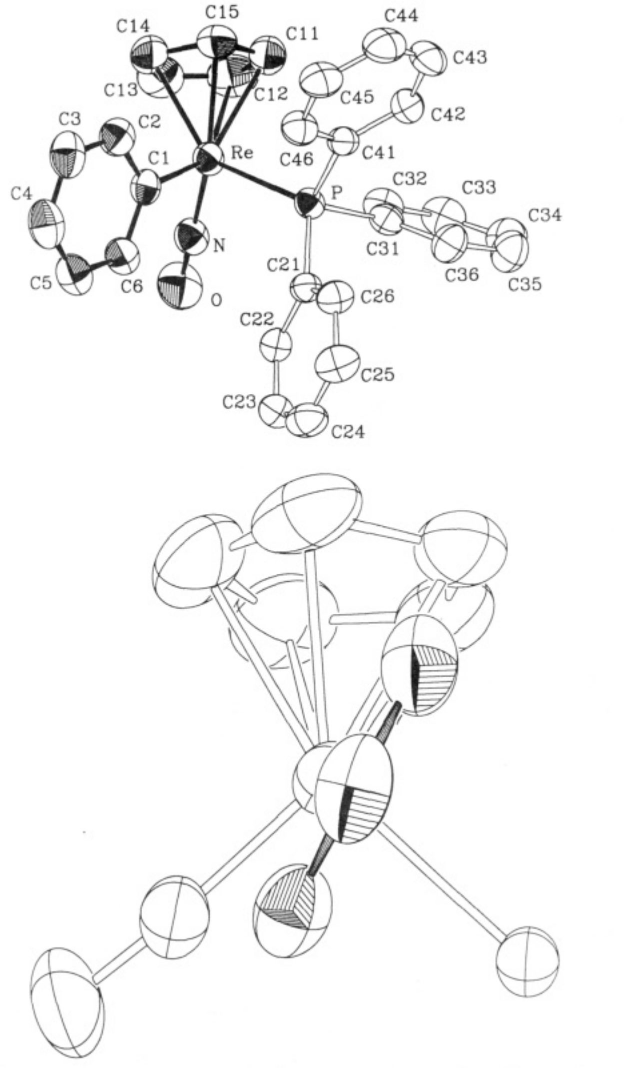
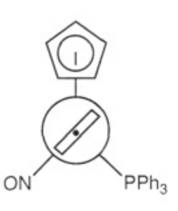


Figure 1. Molecular structure of rhenium phenyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C_6H_5)$ (1): (top) numbering diagram; (bottom) Newman type-projection down the phenyl ligand.

plane. The Re–P and Re–N bonds made angles of 73.9° and −19.6°, respectively, with the least-squares plane.[15] In the reference Re–C_α rotamer shown in Newman projection I, these angles are 90° and 0°, respectively. The d orbital HOMO of the rhenium fragment[3a] $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ is shown in II for comparison.



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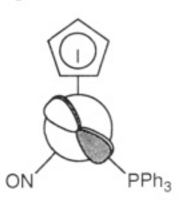
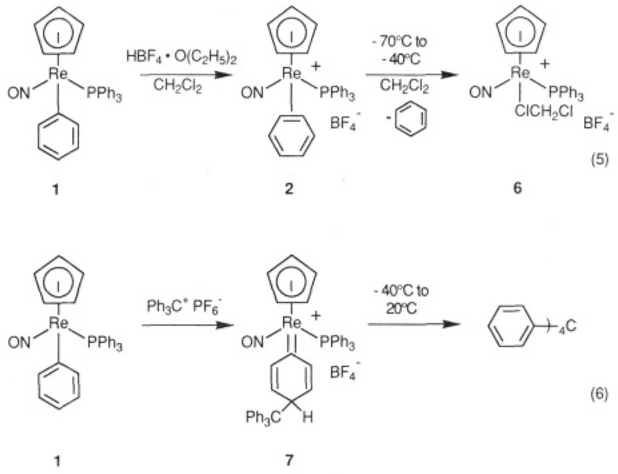


II

2. Reaction of 1 and $HBF_4{\cdot}O(C_2H_5)_2$. Graham found that the carbonyl-substituted phenyl complex $(\eta^5\text{-}C_5H_5)Re(NO)(CO)(C_6H_5)$ can be reversibly protonated by $HBF_4{\cdot}O(C_2H_5)_2$ to the η^2-benzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)(\eta^2\text{-}C_6H_6)]^+BF_4^-$.[7a] This compound exhibited a benzene ligand ^1H NMR resonance at δ 7.23 (s) and was isolable as a powder, but decomposed in dichloromethane above −40 °C.

Scheme III. Reactions of Phenyl Complex 1 with Electrophiles



Accordingly, 1 and $HBF_4{\cdot}O(C_2H_5)_2$ were combined in a NMR tube in CD_2Cl_2 at −80 °C. The sample turned dark red, and ^{31}P and ^1H NMR spectra were recorded at −70 °C. The ^{31}P NMR spectrum showed new resonances at 8.1 (2) and 12.6 ppm (6) in a (72 ± 2):(27 ± 2) area ratio. The ^1H NMR spectrum showed new cyclopentadienyl resonances at δ 5.12 (2) and 5.62 (6) in a (72 ± 1):(27 ± 1) area ratio, a resonance (δ 6.49, s; integrating to ca. six-fifths the area of the δ 5.12 resonance) consistent with a fluxional η^2-benzene ligand, and a minor resonance consistent with free benzene (δ 7.32, overlaped with PPh_3 resonances). A ^{13}C NMR spectrum recorded on a separate sample (−90 °C) showed cyclopentadienyl resonances at 97.3 (2) and 92.2 ppm (6) in a (52 ± 1):(48 ± 1) area ratio, a resonance at 109.7 ppm consistent with a fluxional η^2-benzene ligand ($w_{1/2}$ 6.0 Hz, 1.5 times the $w_{1/2}$ of the cyclopentadienyl resonances), and a resonance consistent with free benzene (127.7 ppm).

When samples were warmed or kept at −70 °C for brief periods, the resonances ascribed to 2 diminished as those of 6 and benzene increased. At −40 °C, conversion to 6 was complete. The NMR properties of 6 were identical with those previously reported for dichloromethane complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$,[5] and an identical set of decomposition products was observed upon warming above −20 °C. Benzene was present in 94 ± 4% yield by ^1H NMR (integration vs internal standard), and its identity was qualitatively confirmed by gas chromatography (following a distillation). Hence, it was concluded that the reaction of 1 and $HBF_4{\cdot}O(C_2H_5)_2$ initially gave the η^2-benzene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}C_6H_6)]^+BF_4^-$ (2), which subsequently underwent solvolysis to 6.

An experiment analogous to the preceding one was conducted in CH_2Cl_2/benzene (0.5 mL/0.3 mL, 1.00:0.42 mol ratio). Some benzene precipitated upon cooling the sample, and a mixture of 2 and 6 formed as above ((54 ± 2):(46 ± 2) by ^{31}P NMR). The sample was warmed to −40 °C, whereupon the conversion of 2 to 6 was complete. The absence of any persistent quantity of 2 strongly suggests that the thermodynamic binding constant of dichloromethane to the rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ is greater than that of benzene.

3. Reactions of 1 with $Ph_3C^+PF_6^-$ and $(CH_3)_3O^+BF_4^-$. In view of the numerous mechanistic possibilities for the reaction of 1 and $HBF_4{\cdot}O(C_2H_5)_2$ (Scheme II and below), we examined reactions of 1 with other electrophiles in hopes of being able to characterize other types of addition

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[15] (a) Selected torsion angles were also computed: P–Re–C1–C6, 79.6°; P–Re–C1–C2, −107.1°; N–Re–C1–C6, −15.2°; N–Re–C1–C2, 168.1°. (b) Sign convention: positive for a clockwise direction of P–Re–C1–C_β, N–Re–C1–C_β, P–Re–phenyl plane, or N–Re–phenyl plane as viewed in Figure 1, bottom.

products. Accordingly, 1 and $Ph_3C^+PF_6^-$ were mixed in CD_2Cl_2 at −80 °C (Scheme III, eq 6). Subsequent ^1H and ^{31}P NMR spectra (−70 °C) showed that one product (7) had cleanly formed.[16] The PPh_3 ^{31}P NMR resonance (16.2 ppm) and cyclopentadienyl ^1H NMR resonance (δ 5.43) were somewhat downfield of those of 2. In a separate experiment, ^{13}C NMR spectra were recorded at −90 and −40 °C.[16c] These showed, in addition to a multitude of phenyl and vinyl carbon resonances,[16c] a markedly downfield resonance (261.3 ppm, d, J_{CP} = 7.5 Hz), a cyclopentadienyl resonance (98.3 ppm), and resonances that could plausibly be assigned to a methine carbon (47.1 ppm) and a quaternary carbon (weak, 61.7 ppm). Some unassigned resonances in the 138–155 ppm range were also evident in the −90 °C spectrum.

Alkylidene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CHR)]^+X^-$ have been shown to exhibit $Re{=}C_\alpha$ ^{13}C NMR resonances in the 285–320 ppm range and ^{31}P NMR resonances in the 16–20 ppm range.[3] Complex 7 also exhibited four ^1H NMR resonances that were consistent with vinyl protons (δ 7.02, 6.85, 6.51, 6.25) and one that was plausible for a methine proton (δ 4.04).[16b] Hence, 7 was assigned as the bis(vinyl)alkylidene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(=CH{-}CH{=}CH{-}CH(CPh_3){-}CH{=}CH)]^+PF_6^-$ derived from para Ph_3C^+ attack on the phenyl ligand.[17]

A sample of 7 was warmed to −40 °C. No change was observed in the ^1H NMR spectrum, but small amounts of decomposition products were noted in the ^{31}P and ^{13}C NMR spectra.[18] The sample was then warmed to −20 °C. The ^{31}P NMR spectrum exhibited a multitude of PPh_3 resonances, and the ^1H NMR spectrum showed that the vinyl and methine resonances had disappeared. The sample was allowed to warm to room temperature. Workup gave tetraphenylmethane in 88% yield, which was characterized by melting point, NMR (^1H, ^{13}C), and mass spectrometry.

Last, similar reactions of 1 and oxonium salt $(CH_3)_3O^+BF_4^-$ (3–5 equiv) were conducted in CD_2Cl_2 at −80 °C. The heterogeneous samples turned dark red, and ^{31}P and ^1H NMR spectra were recorded at −70 °C. In a representative run, the ^{31}P NMR spectrum showed a considerable amount of starting material (19.1 ppm, 23%), resonances consistent with neutral rhenium complexes (19.4, 11%; 18.3, 15%; 17.7, 10%), and resonances consistent with cationic rhenium complexes (12.8, 19%; 12.5, 9%; 12.2, 9%). However, no significant resonances were found in the region of η^2-benzene complex 2 (7.0–9.0 ppm). Although some qualitative features changed, the complexity of this spectrum did not diminish when the sample was warmed. Similarly, the ^1H NMR spectrum showed a multitude of cyclopentadienyl resonances (δ 5.2–5.6, superimposed on a broad hump at δ 5.2), some methyl ether (δ 3.22), and a sharp spike superimposed on the PPh_3 resonances due to a small amount of benzene (δ 7.35). When the sample was warmed, the amount of benzene increased, but toluene did not form in significant amounts (<3%). Complex 1 and $CH_3OSO_2CF_3$ did not react under analogous conditions.

The integrity of the sample of $(CH_3)_3O^+BF_4^-$ was checked by reaction with methoxide complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(OCH_3)$. Clean alkylation to give the methyl ether complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(O(CH_3)_2)]^+BF_4^-$ occurred as previously reported.[19] This reaction is very sensitive to protic impurities in the oxonium salt. Hence, it is concluded that the reaction of 1 and $(CH_3)_3O^+BF_4^-$ is complex and likely involves addition modes other than those observed with $HBF_4{\cdot}O(C_2H_5)_2$ and $Ph_3C^+PF_6^-$.

Discussion

1. Structures of 1 and Other Phenyl Complexes. The crystallization of chiral but racemic compounds in optically active form has abundant precedent.[20] However, it is nonetheless surprising to observe this phenomenon with phenyl complex 1. We have synthesized over 60 complexes of general formula $[(\eta^5\text{-}C_5R_5)Re(NO)(PPh_3)(L)]^{n+}$ (R = H, CH_3; n = 0, 1) in both racemic and optically active form. The racemic complexes are nearly always less soluble and considerably more crystalline, and in most cases the optically active complexes can be isolated only as powders. Yet, for some reason, crystals that contain two molecules of *one* enantiomer of 1 in the unit cell grow faster than those that contain equal numbers of each enantiomer. We have conducted over 40 crystal structures of racemic compounds in this series without previously encountering such an effect.

The $Re{-}C_\alpha$ bond in phenyl complex 1 (2.139 (6) Å) is shorter than those in the corresponding alkyl and allyl complexes (−)-(*R*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2C_6H_5)$, (*SS*,*RR*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH(CH_2C_6H_5)C_6H_5)$, and (*E*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH{=}CHC_6H_5)$ (2.203 (8), 2.215 (4), and 2.192 (6) Å)[2,3a,21] and about the same length as those in vinyl complexes (*E*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}CHCH_2C_6H_5)$ and (*Z*)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C(OCH_3){=}CHCH_2C_6H_5)$ (2.123 (6) and 2.129 (10) Å).[1] These differences can largely be attributed to the bond contraction commonly observed upon replacing an sp^3 carbon by an sp^2 carbon.[22] However, there is the possibility of a contribution from $Re{=}C_\alpha$ multiple bonding involving the d orbital shown in II and ligand acceptor orbitals.[1]

The remaining bond lengths and angles about rhenium in 1 compare closely with previously characterized vinyl, alkyl, and allyl complexes.[1,2,3a,20] The orientation of the phenyl ligand, however, is unusual. On the basis of $Re{-}C_\alpha$ conformations found in the vinyl complexes noted above, the angle of the phenyl ligand least-squares plane with the Re–NO bond would be expected to be 0–40°, as opposed to the −20° found.[15b] In other words, one of the phenyl ligand ortho carbons of 1 (C6) resides in the region between the nitrosyl and PPh_3 ligands in the solid state, as opposed to the region between the nitrosyl and cyclopentadienyl ligands. Previous studies have shown that the former type of interstice is particularly congested,[23] and the importance

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(16) NMR Data: (a) ^{31}P NMR (ppm) 16.2 (s, PPh_3), −144.0 (sept, J_{PF} = 712 Hz, PF_6^-). (b) ^1H NMR (δ) 7.18–7.08 (m, 6 C_6H_5), 7.02 (br d, J = 7.22 Hz, 1 H), 6.85 (br d, J = 9.94 Hz, 1 H), 6.51 (br d, J = 8.7 Hz, 1 H), 6.25 (br d, J = 8.8 Hz, 1 H), 5.43 (s, C_5H_5), 4.04 (br s, 1 H). (c) ^{13}C NMR (ppm, −40 °C) 261.3 (d, J_{CP} = 7.5 Hz, $Re{=}C_\alpha$); vinyl CH (s) at 147.7, 145.9, 136.8, 136.5; PPh_3 at 132.6 (d, J = 10.7 Hz), 132.0 (s), 130.4 (d, J_{CP} = 60.5 Hz), 129.2 (d, J = 11.4 Hz); C*Ph* (s, tentative assignments) at 130.2, 128.6, 127.8, 127.6; 98.3 (s, C_5H_5, 89%); other C_5H_5 at 110.9, 3%; 97.4, 2%; 97.0, 4%; 92.4, 1%; 92.0, 1%); 61.7 (s, *C*C_4), 47.1 (s, CH).

(17) (a) The present data do not rigorously exclude the alkylidene complex that would be derived by ortho Ph_3C^+ attack upon the phenyl ligand of 1 as the structure of 7. However, we believe this possibility is less likely on steric grounds. (b) $Re{=}C_\alpha$ bond rotation in 7 is expected to be slow in the temperature regime of these experiments.[3] Hence, two stereoisomers of 7, which differ in the direction of $Ph_3C^+PF_6^-$ attack upon 1 (syn vs anti to the bulky PPh_3 ligand), are possible. The NMR data suggest that the reaction is stereospecific.

(18) ^{31}P NMR (ppm), −40 °C: 16.2 (7), 87%; 12.6 (6), 5%; 9.7, 4%; 9.1, 4%. −20 °C: many peaks at 20.9–15.8, 35%; 12.9, 60%; 12.0, 5%.

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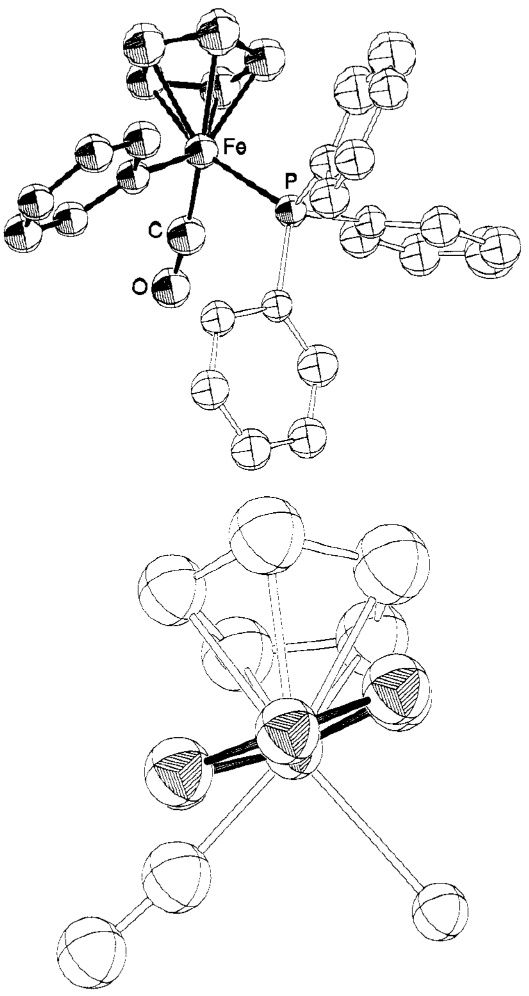

Figure 2. Molecular structure of iron phenyl complex $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(C_6H_5)$: (top) full view; (bottom) Newman-type projection down the phenyl ligand.

of M–C_α conformers that direct carbon substituents into this area has been discounted. Unfortunately, there is no obvious method to assay whether the Re–C_α conformation of 1 observed in the solid state also dominates in solution.

A computer search of the Cambridge crystallographic data base located 127 structurally characterized transition metal–phenyl complexes. These included a 14-valence-electron rhenium phenyl complex, $(Et_2PhP)_2Re(C_6H_5)_3$ (8),[24] and two cyclopentadienyliron complexes that are "isoelectronic" with 1, $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(C_6H_5)$ (9) and $(\eta^5\text{-}C_5H_5)Fe(CO)(\overline{P(-OCH_2CH_2-)_2N})(C_6H_5)$ (10).[25,26] The Re–C_α bonds in 8 (2.029 (10)–2.024 (11) Å) are markedly shorter than those in the 18-valence electron complex 1 and other reference compounds.[24] Accordingly, Re–C_α π bonding was proposed to account for this diminution.[24] The M–C_α bonds in iron complexes 9 and 10 (2.11, 2.037 (5) Å) are somewhat shorter than that in 1, as is commonly found when comparing related first-row and third-row transition-metal complexes.

Except for shortened metal–ligand bonds, the iron phenyl complex $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(C_6H_5)$ (9) can be considered "isosteric" with 1. Hence, solid-state structures were generated from published atomic coordinates (Figure 2).[25] Interestingly, the M–C_α conformation differs considerably from that in 1. The least-squares plane of the phenyl ligand was calculated and was found to make angles of 26.3° and 113.1° with the Fe–CO and Fe–PPh_3 bonds, respectively.[15b] Hence, the planes of the phenyl rings in 1 and 9 differ by 40–45° out of a possible maximum of 90° for orthogonal orientations. Attempts have been made to apply a common set of guidelines for ligand conformations in corresponding $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(X)$ complexes.[23] However, these data indicate that substantial differences are possible.

In these types of rhenium and iron complexes, it is common to observe one of the PPh_3 ligand phenyl rings in a plane roughly parallel to that defined by C_α, the metal, and the NO or CO ligand. Such a feature is conspicuously absent in 1. We speculate that M–C_α conformations in which the phenyl ligand eclipses the M–NO or M–CO bonds (e.g., I) may be slightly destabilized by a steric interaction involving an ortho hydrogen. This is relieved by a ca. 20° twist of the M–C_α bond in either direction. However, this in turn generates in 1 a close contact (ca. 2.9 Å) between the other ortho hydrogen and cyclopentadienyl hydrogens.

2. Syntheses and Properties of η^2-Benzene Complexes. In the period since Graham reported the synthesis of $[(\eta^5\text{-}C_5H_5)Re(NO)(CO)(\eta^2\text{-}C_6H_6)]^+BF_4^-$,[7a] additional η^2-benzene complexes have been isolated.[8,9] These include $[Os(NH_3)_5(\eta^2\text{-}C_6H_6)]^{2+}2CF_3SO_3^-$ and several species in which two metals bind anti and η^2 to the same benzene ring.[8,9] The complexes $(\eta^5\text{-}C_5Me_5)Re(CO)_2(\eta^2\text{-}C_6H_6)$ and $(\eta^5\text{-}C_5H_5)Rh(PMe_3)(\eta^2\text{-}C_6H_6)$ have been detected spectroscopically.[8a,10] Interestingly, all of these syntheses except Graham's and ours utilize large excesses of *free* benzene.

Benzene is readily displaced from all of the preceding complexes by weak donor ligands. Indeed, our data show that benzene likely has a much poorer thermodynamic binding constant than dichloromethane for the rhenium fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$. Together with other studies,[19] the following basicity order toward $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ is now established: $RCH{=}CH_2 > R_2O > CH_2Cl_2 > C_6H_6$. In other work, we have found that the chlorobenzene ligand in $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(ClC_6H_5)]^+BF_4^-$ chiefly binds to rhenium through chlorine, but other isomeric species, possibly η^2-arene complexes, are evident by ^{31}P NMR.[27]

Jones has obtained elegant evidence for the intermediacy of $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(\eta^2\text{-}C_6H_6)$ (11, Rh(I)) in benzene activation reactions that lead to $(\eta^5\text{-}C_5Me_5)Rh(PMe_3)(H)(C_6H_5)$ (12, Rh(III)).[6] No evidence is seen for a similar conversion of 2 to phenyl hydride complex 4 (Scheme II). We presume that such Re(I) → Re(III) oxidative additions are less favorable thermodynamically than unbiquitously observed Rh(I) → Rh(III) oxidative additions. Naphthalene and phenanthrene analogues of 11 have recently been isolated.[28]

Unfortunately, phenyl complex 1 and $HBF_4\cdot O(C_2H_5)_2$ react too rapidly in dichloromethane to allow the detection of intermediates by conventional NMR methods. In principle, 2 might form in a single step without intermediates via proton attack on the Re–C_α σ bond. However, there are two limiting alternatives. First, the proton could attack the carbon terminus of the Re–C_α bond (ipso attack) to give the delocalized carbocation 3 (Scheme II), one resonance form of which would have a positive charge on C_β. Collapse to π-complex 2 would then be anticipated.

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Second, the proton could attack the rhenium terminus of the Re–C_α bond to give phenyl hydride complex **4** (Scheme II). A reductive elimination/migration sequence, possibly involving a σ-bond complex,[29] could then lead to **2**. There are numerous more exotic possibilities. For example, the ortho (C_β) or para (C_δ) carbons could be protonated to alkylidene complexes such as **5** (Scheme II). These could undergo 1,2- or 1,4-hydride migrations of the type previously observed to convert alkylidene complexes to η^2-alkene complexes.[30] Finally, all of these modes of electrophilic addition could occur reversibly, regardless of the mechanism that leads to **2**.

The reaction of **1** and $Ph_3C^+PF_6^-$ (Scheme III) provides to our knowledge the first observable example of electrophilic addition to a phenyl ligand to give an alkylidene ligand. Since $Ph_3C^+PF_6^-$ does not add to free benzene, the $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)$ moiety can be viewed as an activating substituent. Similar carbon–carbon bond-forming reactions, analogous to the carbon–hydrogen bond-forming reactions in Scheme I, occur when vinyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH{=}CHR)$ and allyl complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH{=}CHR)$ are treated with $Ph_3C^+PF_6^-$.[1,4b] However, it should be emphasized that there is a strong possibility that these transformations entail initial electron transfer.[31] Thus, the actual addition step may involve $\mathbf{1}^{\bullet+}$ and the attacking *radical* $Ph_3C^\bullet$.

The decomposition of alkylidene complex **7** to tetraphenylmethane is presumed to involve an η^2-tetraphenylmethane complex, the formation of which would require some type of carbon–hydrogen or carbon–carbon bond cleavage. Conceivably, the addition of $Ph_3C^+PF_6^-$ might be reversible, allowing a number of mechanistic possibilities. The oxonium salt $(CH_3)_3O^+BF_4^-$ certainly reacts much less cleanly with **1** than either $HBF_4{\cdot}O(C_2H_5)_2$ or $Ph_3C^+PF_6^-$. Possible factors include reaction heterogeneity (which could promote independent reactions of **1** and initial products) and a lowered electron transfer equilibrium.

3. Summary.

This study has extended earlier syntheses of aryl complexes to compounds of the formula $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Ar)$, uncovered an unexpected kinetic resolution and solid-state aryl ligand conformation, and established two modes of aryl ligand electrophilic addition, one of which appears to be stereospecific.[17b] Future reports will extend this series of studies with unsaturated hydrocarbon ligands[1–4] to alkyne complexes[32] of the formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(RC{\equiv}CR')]^+BF_4^-$ and describe continued investigations of the types of species shown in Scheme II.

Experimental Section

General Methods. All reactions were conducted under a dry N_2 atmosphere. FT-IR spectra were recorded on Perkin-Elmer 1500 and Mattson Polaris spectrometers. NMR spectra were recorded on Varian XL spectrometers and referenced as follows: ^{31}P NMR, external 85% H_3PO_4; ^1H NMR, $CDHCl_2$ at δ 5.32, $CHCl_3$ at δ 7.24, or C_6D_5H at δ 7.15; ^{13}C NMR, CD_2Cl_2 at 53.8 ppm or C_6D_6 at 128.0 ppm. Microanalyses were conducted by Atlantic Microlab, Norcross, GA.

Solvents and reagents were purified as follows: CH_2Cl_2, distilled from P_2O_5 or CaH_2; tetrahydrofuran and benzene, distilled from Na/benzophenone; hexane, distilled from sodium; $CDCl_3$ and CD_2Cl_2, vacuum transferred from CaH_2; $HBF_4{\cdot}O(C_2H_5)$ (Aldrich), standardized as previously described;[5] $Ph_3C^+PF_6^-$ (Columbia), dissolved in a minimum of CH_2Cl_2, precipitated with ethyl acetate, and washed with hexane; C_6H_5MgBr (Aldrich), $(CH_3)_3O^+BF_4^-$ (Alfa), and $CuBr{\cdot}S(CH_3)_2$ (Aldrich), used as received.

Preparation of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(C_6H_5)$ (1). A Schlenk flask was charged with $CuBr{\cdot}S(CH_3)_2$ (0.823 g, 4.00 mmol), THF (20 mL), and a stir bar. The suspension was cooled to 0 °C and C_6H_5MgBr (0.443 mL, 1.33 mmol; 3.0 M in ether) was slowly added.[12] The reaction was stirred for 30 min and turned yellow-brown. Then a solution of $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(Cl)$ (0.716 g, 1.24 mmol)[13] in THF (12 mL) was added. The suspension was stirred at 0 °C for 1.5 h and then poured through a fritted glass funnel containing a 2–3-cm layer of Celite. Solvent was removed from the dark orange filtrate by rotary evaporation. The residue was extracted with CH_2Cl_2, and the extract was filtered through a fritted glass funnel containing a 2-cm layer of silica gel. Solvent was removed from the filtrate, and the residue was dissolved in a minimum of CH_2Cl_2. Hexane was added. This gave a red-orange powder, which was collected by filtration, washed with hexane, and vacuum dried to give **1** (0.632 g, 1.02 mmol, 82%) as an orange powder, mp 196–198 °C, dec. Anal. Calcd for $C_{29}H_{25}NOPRe$: C, 56.11; H, 4.06; N, 2.26. Found: C, 55.50; H, 4.12; N, 2.22. A sample was dissolved in CH_2Cl_2, and a layer of hexane was added. Orange prisms slowly formed, which were collected by filtration and dried under vacuum. Anal. Found: C, 55.93; H, 4.07; N, 2.25.

Spectroscopic data: IR (cm^{-1}, ν_{NO}) $CHCl_3$, 1645 s; KBr, 1633 s. ^1H NMR ($CDCl_3$) 300 MHz δ 7.32 (m, 3 C_6H_5), 7.12 (m, 2 H), 6.70 (m, 2 H), 6.60 (m, 1 H), 5.13 (s, C_5H_5); 400 MHz δ 7.37 (m, 3 C_6H_5), 7.15 (d, J = 8 Hz, 2 H_o), 6.69 (dd, J = 7 Hz, 7 Hz, 2 H_m), 6.55 (dd, J = 7 Hz, 7 Hz, 1 H_p), 5.15 (d, J = 2 Hz, C_5H_5). $^{13}C\{^1H\}$ NMR (ppm, $CDCl_3$) 75 MHz $P(C_6H_5)_3$ at 135.4 (d, J = 54 Hz, ipso), 133.5 (d, J = 11 Hz), 129.7 (s, *p*), 127.9 (d, J = 10 Hz); ReC_6H_5 at 142.3 (d, J = 9 Hz, ipso), 142.1 (s, *o*), 126.0 (s, *m*), 120.4 (s, *p*); 91.9 (s, C_5H_5); 100 MHz $P(C_6H_5)_3$ at 135.9 (d, J = 53 Hz, ipso), 133.8 (d, J = 10 Hz), 130.1 (d, J = 2 Hz, *p*), 128.2 (d, J = 10 Hz); ReC_6H_5 at 143.0 (d, J = 10 Hz, ipso), 142.4 (s, *o*), 126.3 (s, *m*), 120.5 (s, *p*); 91.8 (d, J = 2 Hz). $^{31}P\{^1H\}$ NMR (ppm, $CDCl_3$) 20.3 (s). Mass spectrum (17 eV, *m/e*, ^{187}Re) 621 (M^+, 100%), 545 ($M^+ - C_6H_5$, 2%), 359 ($M^+ - PPh_3$, 3%), 262 (PPh_3^+, 10%).

Reaction of 1 and $HBF_4{\cdot}O(C_2H_5)_2$. A 5-mm NMR tube was charged with **1** (0.50 g, 0.08 mmol) and CD_2Cl_2 (0.6 mL) and was capped with a septum. The tube was cooled to −80 °C, and $HBF_4{\cdot}O(C_2H_5)_2$ (11 μL, 0.08 mmol) was added by syringe. The tube was shaken, and the orange solution turned dark red. The tube was transferred to a −70 °C NMR probe, and data were acquired as described in the text.

Reaction of 1 and $Ph_3C^+PF_6^-$. A 5-mm NMR tube was charged with **1** (0.062 g, 0.100 mmol) and $Ph_3C^+PF_6^-$ (0.039 g, 0.100 mmol) and capped with a septum. The tube was cooled to −80 °C and CD_2Cl_2 (0.6 mL) was added by syringe. The tube was shaken to give a yellow-green solution and transferred to a −70 °C NMR probe. For data, see text.[16] A more concentrated sample (0.163 mmol in 0.6 mL of CD_2Cl_2) was prepared for ^{13}C NMR analysis.

The preceding sample was kept at room temperature for 2 days. It turned brown, and volatiles were removed under oil pump vacuum. The residue was extracted with benzene (25 mL). The extract was filtered twice through fritted glass funnels containing 2-cm layers of silica gel. Solvent was removed from the colorless filtrate by rotary evaporation. The resulting white powder was dried under vacuum to give tetraphenylmethane (0.046 g, 0.144 mmol, 88%), mp 283–284 °C (lit.[33] mp 285 °C). ^1H NMR (C_6D_6, 60 °C) δ 7.36–7.28 (m, 8 H), 7.13–6.92 (m, 12 H). ^{13}C NMR (ppm, C_6D_6, 60 °C) 147.4 (s, ipso), 131.7 (s, *o*), 127.8 (s, *m*), 126.2 (s, *p*), quaternary carbon not detected. Mass spectrum (*m/e*, 70 eV) 320 (M^+, 38%), 243 ($M^+ - C_6H_5$, 100%), 165 ($M^+ - C_{12}H_{11}$, 65%).

Reaction of 1 and $(CH_3)_3O^+BF_4^-$. A 5-mm NMR tube was charged with **1** (0.064 g, 0.103 mmol) and $(CH_3)_3O^+BF_4^-$ (0.078 g, 0.527 mmol) and capped with a septum. The tube was cooled to −80 °C, and CD_2Cl_2 (0.6 mL) was added by syringe. The tube was shaken to give a dark red heterogeneous suspension. For data, see text.

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Crystal Structure of 1. Data were collected on a Syntex P$\bar{1}$ diffractometer as outlined in Table I. The unit cell was determined by using 15 centered reflections with 9° < 2θ < 25°. The structure was solved with standard heavy-atom techniques, using the UCLA Crystallographic Package. Programs used have been previously detailed.[34] The structure was refined to convergence at an R value of 0.031 (R_w = 0.040). Since molecules in polar space groups can give somewhat inaccurate heavy-atom positions if the incorrect enantiomer is chosen,[35] the atomic coordinates of all atoms were multiplied by −1 to give the enantiomeric molecule, which was refined further. The R value dropped to 0.028 (R_w = 0.035), indicating the enantiomeric molecule (R absolute configuration) to be present in the crystal. All data compiled correspond to (R)-1.

Acknowledgment. We thank the Department of Energy for support of this research and A. M. Arif and M. A. Dewey for assistance with the structural data.

Supplementary Material Available: Table of anisotropic thermal parameters for 1 (1 page); a table of calculated and observed structure factors for 1 (26 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Reactivity of Chiral Rhenium Alkene Complexes of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHR)]^+X^-$

Gerardo S. Bodner, Tang-Sheng Peng, Atta M. Arif, and J. A. Gladysz*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received September 27, 1989

Reaction of the dichloromethane complex $[(\eta\text{-}C_5H_5)Re(NO)(PPh_3)(ClCH_2Cl)]^+BF_4^-$ and monosubstituted alkenes gives $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHR)]^+BF_4^-$ (**3**$^+BF_4^-$, 89–91%; R = CH_3 (**a**), n-C_3H_7 (**b**), $CH_2C_6H_5$ (**c**), C_6H_5 (**d**)) as (73–62):(27–38) mixtures of (*RS*,*SR*)/(*RR*,*SS*) diastereomers. Reactions of η^1-allyl complexes (E)-$(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CH_2CH{=}CHR')$ (**4**; R′ = H (**a**), C_6H_5 (**c**)) and electrophiles E^+X^- ($E^+ = H^+, D^+, R^+$) give alkene complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CHCHER')]^+X^-$ (79–92%) as (75–60):(25–40) mixtures of diastereomers. When (*RS*,*SR*)/(*RR*,*SS*)-**3a–c**$^+BF_4^-$ are heated (C_6H_5Cl, 95–100 °C), they equilibrate to ≃95:5 mixtures of diastereomers. Rationales are given for the modest kinetic and high thermodynamic stereoselectivities. The crystal structure of independently synthesized (*RR*,*SS*)-**3c**$^+PF_6^-$ shows the =CHR alkene terminus to be approximately anti to the PPh_3 ligand, with R syn to the C_5H_5 ligand. NOE experiments show that the =CHR terminus is anti to the PPh_3 ligand in both diastereomers of **3**$^+X^-$ in solution. Variable-temperature ^{13}C NMR spectroscopy gives $\Delta G^{\ddagger}_{369\,K}$ = 16.4 kcal/mol for Re–(C⌐C) rotation in the ethylene complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(H_2C{=}CH_2)]^+PF_6^-$. Also described are substitution reactions of **3**$^+X^-$, a detailed analysis of the spectroscopic properties of **3**$^+X^-$, and high 1,4-asymmetric induction in the reaction of **4c** and CF_3SO_3D to give **3c**-$d_1$$^+CF_3SO_3^-$.

Introduction

There is an extensive chemistry of transition-metal alkene complexes, the history of which dates back to the origins of organometallic chemistry.[1] There are also numerous chiral metal complexes that catalyze asymmetric reactions of alkenes.[2] Over the last dozen years, a variety of chiral-at-metal alkene complexes have been synthesized in optically active form.[3,4] However, applications of such complexes in asymmetric organic synthesis have not been extensively developed. For example, it should be possible to design chiral transition-metal receptors that can selectively bind and activate one enantioface of prochiral alkenes.

We have undertaken an extensive study of easily resolved,[5] chiral-at-metal rhenium complexes of the formula $[(\eta^5\text{-}C_5R_5)Re(NO)(PPh_3)(L)]^+X^-$.[6] The pyramidal 16-valence-electron fragment $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ possesses the high-lying d donor orbital shown in I (Scheme I),[7] and hence the Dewar–Chatt–Duncanson model[8] predicts the formation of alkene complexes with the general Re—C⌐C conformation in II. Monosubstituted alkenes $H_2C{=}CHR$ can give two diastereomeric complexes (*RS*,*SR* and *RR*,*SS*)[9] that differ in the alkene enantioface bound

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