We thank Petra Kollat for assistance in structural investigations.

Registry No. **1a**, 16857-93-5; **1b**, 20758-47-8; **1c**, 20758-48-9; **1d**, 16857-95-7; **1e**, 16857-99-1; **2a**, 95421-47-9; **2b**, 95464-51-0; **2c**, 95421-48-0; **2d**, 95421-49-1; **2e**, 95421-50-4; **3**, 76862-03-8; **4a**, 95421-51-5; **4b**, 95421-52-6; $Cr(CO)_6$, 13007-92-6; $LiC(CH_3)_2CN$, 50654-53-0; [(trimethylsilyl)benzene]TCC, 33248-13-4; benzaldehyde, 100-52-7; 2-methylpropionitrile, 78-82-0; (3-benzoylphenyl)acetonitrile, 21288-34-6; 2-(3-benzoylphenyl)-2-methylpropionitrile, 60566-76-9.

Supplementary Material Available: Listings of structure factor amplitudes, hydrogen atom parameters, anisotropic temperature factors, and equations for least squares planes (183 pages). Ordering information is given on any current masthead page.

Control of Slippage and Conformation in Indenyl Complexes

J. W. Faller,* R. H. Crabtree,* and A. Habib

Department of Chemistry, Yale University, New Haven, Connecticut 06511

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A systematic approach and rationalization of the departure of cyclopentadienyl groups from the classical symmetrical η^5-arrangement is presented. Slippage of the metal from the center to one side of the five-membered ring is shown to be a common occurrence. Furthermore, the direction of the slippage and the conformation of the indenyl ring relative to the other substituents on the metal can be predicted by using simple trans effect arguments. The effects of slippage and conformation on NMR parameters are illustrated. The structures of two complexes were determined by X-ray crystallographic analysis. Crystal data for $(\eta^5\text{-}C_9H_7)Mo(CO)_2(\eta^2\text{-}1\text{-}CH_3C_3H_4)$: space group $P2_1/n$; $a = 11.978$ (3) Å, $b = 7.992$ (1) Å, $c = 14.109$ (4) Å; $\beta = 91.85$ (3)°; $V = 1350.1$ (9) Å^3; $M_r = 322.22$; $Z = 4$; $\rho_{calcd} = 1.59$ g cm^{-3}. For 1364 reflections with $F^2 \geq 3\sigma(F^2)$, $R_1 = 0.033$ and $R_2 = 0.034$. Crystal data for $[(\eta^5\text{-}C_9H_7)IrH\{P(C_6H_5)_3\}_2]BF_4\cdot CH_2Cl_2$: space group $P2_1/n$; $a = 12.895$ (2) Å, $b = 12.285$ (3) Å, $c = 26.566$ (6) Å; $\beta = 94.08$ (2)°; $V = 4198$ (3) Å^3; $M_r = 1004.69$; $Z = 4$; $\rho_{calcd} = 1.59$ g cm^{-3}. For 3717 reflections with $F^2 \geq 3\sigma(F^2)$, $R_1 = 0.046$ and $R_2 = 0.054$.

In this paper we attempt to systematize and rationalize the departure of cyclopentadienyl groups from the classical symmetrical η^5-arrangement. Such departures are important because they represent a way of producing coordinative unsaturation and thus enhancing the reactivity of η^5-cyclopentadienyl complexes. For example, the rates of substitution reactions of some coordinatively saturated η^5-indenyl complexes are rapid compared with their η^5-cyclopentadienyl analogues.[1-4] This has been attributed to the ease of slippage of the metal from the center of the ring to one side and the formation of a more reactive η^3-indenyl intermediate. The sideways displacement of the metal is presumably facilitated in the indenyl complex by the recovery of some of the resonance energy in the benzene ring.

As early as 1966, the second-order component of the rate expressions for carbonyl substitution by phosphine in η^5-CpRh$(CO)_2$ was attributed to formation of a η^4-Cp intermediate.[3] Renewed interest in slippage from η^5-Cp to η^3-Cp and eventually conversion to the η^1-Cp complex has arisen owing to recent observations that treatment of η^5-CpMo$(CO)_2$(NO), η^5-CpW$(CO)_2$(NO), η^5-CpRe$(CO)_3$, and η^5-CpRe(CO)(NO)(CH_3) gave η^1-Cp products rather than carbonyl substitution upon treatment with Me_3P.[5-10]

Although the existence of the η^3-Cp group had previously been suggested to be mythical[11] or to not correspond to a plausible molecular state,[12] the X-ray structure of (η^5-Cp)W$(CO)_2$(η^3-Cp) showed conclusively that an unambiguously η^3-Cp structure could exist as an isolable species.[13] A key feature in the (η^5-Cp)W$(CO)_2$(η^3-Cp) structure is the folding of the uncomplexed C=C fragment out of the plane of the the allyl fragment to produce an *envelope angle* of $\Omega = 20°$. It is this folding of the C_5 ring that provides one approach to assigning η^3-character to a system. As the five-membered ring flattens, the unequivocal distinction between an η^5- and an η^3-Cp fades[11,12] and delineation as one of these extremes becomes unwarranted. Nevertheless, small distortions from five-fold symmetry occur in η^5-Cp complexes which can be rationalized by electronic effects arising from the other ligands on the metal.[14]

The resonance energy gained in the distortion to a allyl–ene type five-membered ring in indenyl complexes has a profound effect on their chemistry and the stability of various conformations of the ring relative to the other ligands on the metal. The question of conformational

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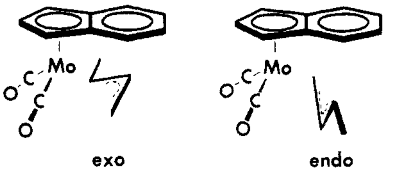
preferences in a variety of substituted rings has been addressed in a number of recent studies[15-22] and is of potential interest in controlling regiochemistry of reactions on the rings.

Some of the more unusual effects of preferred geometries in indenyl complexes are the extraordinarily large ring-current shifts produced by the six-membered ring. These large shifts occur when a preferred conformation results in the benzene ring being held predominently in a position over a proton in another ligand in the complex.[22] We report here some examples of slipped indenyl rings, the effects of their preferred conformation, and a rule of thumb for predicting and rationalizing the direction of slippage and the preferred orientation.

Results

$(\eta^5\text{-In})Mo(CO)_2(\eta^3\text{-}C_4H_7)$. The effects of preferred conformation of an indenyl ligand can most readily be observed in NMR spectra. In the case of *exo*-(η^5-indenyl)Mo(CO)$_2$(η^3-crotyl), for example, the central proton on the allylic portion of the η^3-crotyl ligand is shifted upfield by 3.38 ppm compared to the η^5-Cp analogue[22] (**I**).



There are two conformers in solution which differ in the orientation of of the allyl moiety, and both show shifts indicative of an indenyl conformation which holds the aromatic ring over the allylic moiety. This is illustrated in Figure 1, which clearly shows the upfield shifts of the anti protons in the endo conformer and the central proton in the exo conformer. It is the magnetic anisotropy of the six-membered ring which gives rise to the large upfield shifts of the protons in the η^5-indenyl complex.

There is a moderately rapid equilibration ($k_{\text{exo-endo}} = 20$ s^{-1}) of the exo and endo isomers at room temperature and crystallization results in isolation of only the exo isomer, the structure of which is shown in Figure 2. Thus, in the solid, the preferred orientation of the benzene ring over the allyl moiety is maintained, as expected on the basis of the ring-current effects in solution. It should be noted that the magnitude of the shifts require that the ring be over the allyl most of the time but does not demand that the indenyl ring be locked into that orientation.[22]

$\{(\eta^5\text{-Indenyl})Ir[P(C_6H_5)_3]_2H\}BF_4$. The ^{1}H NMR spectrum of the phenyl protons in $\{(\eta^5\text{-In})Ir[P(C_6H_5)_3]_2H\}BF_4$ show an unusual upfield shift (Figure 3). This can be attributed to the ring-current effect of the indenyl ligand with a preferred orientation of the six-membered ring over the phenyl group. The upfield shift of all of the ortho protons of the triphenylphosphine indicates rapid rotation about the P–C and P–Ir bonds on the NMR time scale.

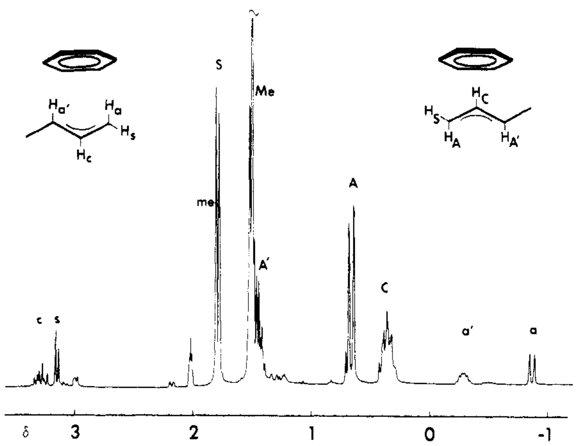


Figure 1. The 500-MHz ^{1}H NMR spectrum of (η^5-In)Mo(CO)$_2$(η^3-C$_4$H$_7$) in CDCl$_3$ at 0 °C.

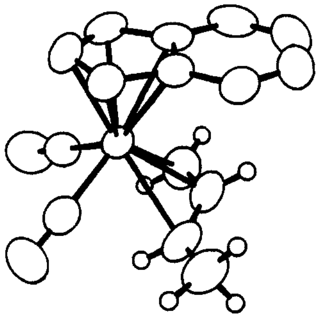


Figure 2. An ORTEP diagram of *exo*-(η^5-In)Mo(CO)$_2$(η^3-C$_4$H$_7$) showing 50% probability ellipsoids for the non-hydrogen atoms. Hydrogen atoms of the allyl group are shown in calculated positions.

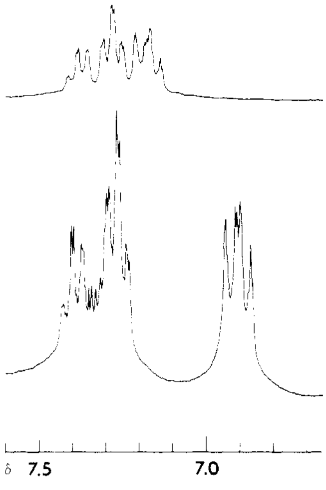


Figure 3. A comparison of the 250-MHz ^{1}H NMR spectra of $\{(\eta^5\text{-Cp})Ir[P(C_6H_5)_3]_2H\}BF_4$ and $\{(\eta^5\text{-indenyl})Ir[P(C_6H_5)_3]_2H\}BF_4$ in CD$_2$Cl$_2$. The spectrum of the indenyl compound is given in the lower trace.

A second indication of a preferred orientation can be found in the ^{13}C NMR spectra of this compound which only shows a significant splitting (6 Hz) from ^{31}P coupling in the C-1 and C-3 carbons of the indenyl ring.

Discussion

Preferred Ring Orientation. The preferred conformation of the indenyl ligand relative to the ML$_2$L′ fragment is such that the ligands with the greatest trans in-

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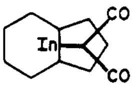
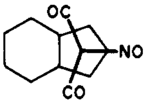
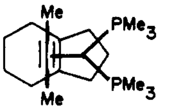
Chart I



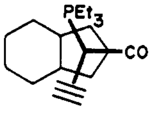
$(\eta^5\text{-In})W(CO)_2(\eta^5\text{-In})$[23]



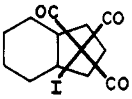
$(\eta^5\text{-In})Cr(CO)_2(NO)$[24]



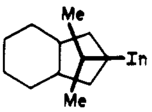
$[(\eta^5\text{-In})Mo(PMe_3)_2(MeC_2Me)]BF_4$[25]



$[(\eta^5\text{-In})Mo(PEt_3)(CO)(MeC_2Me)]BF_4$[25]

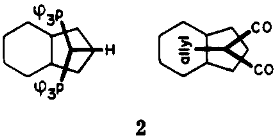


$(\eta^5\text{-In})Mo(CO)_3I$[26]



$(\eta^5\text{-In})_2M(Me)_2$, M = Ti, Zr, Hf[27]

fluence are trans to the six-membered ring. In $\{(\eta^5\text{-In})Ir[P(C_6H_5)_3]_2H\}BF_4$ the hydride is trans to C(8) and C(9) of the indenyl ring. In $(\eta^5\text{-In})Mo(CO)_2(\eta^3\text{-}C_4H_7)$ the two carbonyls, which each have greater trans influence than allyl share the side trans to C(8)–C(9), (2). The same



2

effect occurs in several other structures, although they were not rationalized in this manner in the original reports (Chart I). The driving force for adopting this conformation must be the the greater degree of recovery of resonance energy in the benzenoid ring when the ligand of greater trans influence is trans to C(8)–C(9). When this happens, the M–C(8) and M–C(9) bond lengths increase (~8% in the iridium case), partially releasing the carbon p orbitals on C(8) and C(9) from their involvement with the metal and allowing them to interact to a greater extent with the other benzenoid carbon atoms C(4)–C(7). Thus, the strongest bonds to the five-membered ring are maintained trans to the ligands with the weakest trans influence.

Ring Slippage. In all structures published to date, the metal atom in an η^5-indenyl complex appears to have undergone a slip distortion, usually in the direction of C(2). This is clearly evident in Figures 4 and 5 which show a view down the normal to the plane of the five-membered ring in both cases. Several methods[27,28] have been suggested for describing this slip distortion; the one described by Mingos[28] for analogous distortions in carbametallaboranes being particularly attractive for our purposes.

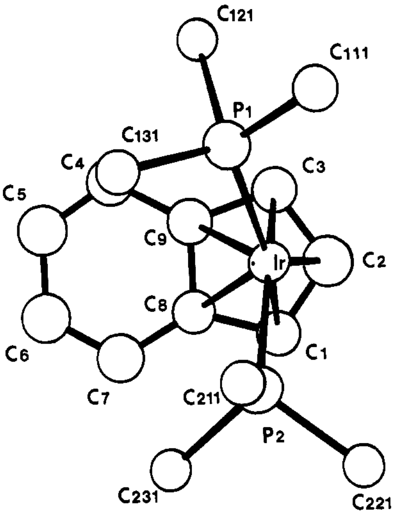


Figure 4. An ORTEP view of the $\{(\eta^5\text{-In})Ir[P(C_6H_5)_3]_2H\}^+$ ion along the normal to the plane of the five-membered ring. The centroid of the ring is indicated by a dot.

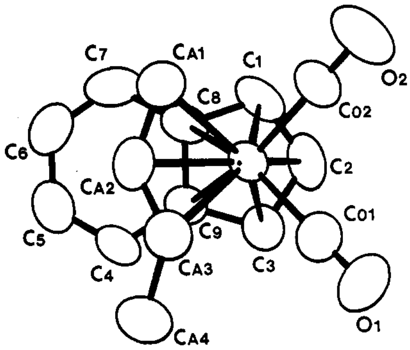


Figure 5. An ORTEP view of the $(\eta^5\text{-In})Mo(CO)_2(\eta^3\text{-}C_4H_7)$ along the normal to the plane of the five-membered ring. The centroid of the ring is indicated by a dot.

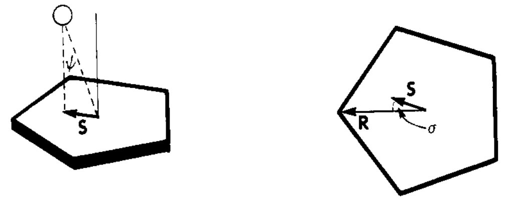


Figure 6. Definitions of slip vector, **S**, and slip angle, σ.

The slip distortion, Δ, is defined as the distance from the normal of a reference plane to the metal atom, this normal passing through the centroid of the five-membered ring. The most obvious reference plane is that of the five-membered ring. In order to calculate this distortion and provide an indication of the direction of the distortion, we will define the slip vector, **S**, as a vector connecting the projection of the five-membered ring centroid and the projection of the metal atom on the plane. The length of this vector is Δ. The angle it makes with the reference vector **R** where **R** is the vector from the projection of the centroid to the projection of the unique ring atom C(2) is

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Table I. Slip Parameters for Indenyl and Cyclopentadienyl Complexes

compound	slip parameters					
	$\Delta = \lvert S \rvert$, Å	σ, deg	ψ, deg	$\overline{\Delta M\text{–}C}$, Å	Ω, deg	ref
$CpMo(CO)_2(endo\text{-}\eta^3\text{-}2\text{-}MeC_3H_4)$	0.079	31.8	2.2	0.04[a]	1.5	34
$CpMo(CO)_2(exo\text{-}\eta^3\text{-}C_6H_9)$	0.067	0.0	1.9	0.05[a]	0.2	35
$CpMo(CO)_2(exo\text{-}\eta^3\text{-}C_7H_{11})$	0.098	8.3	2.8	0.08[a]	1.5	34
$(\eta^5\text{-}Cp)W(CO)_2(\eta^3\text{-}Cp)$ $[\eta^5]$	0.076	0.0	2.2	0.10	(4.9)[b]	13
$[\eta^3]$	0.928	0.0	23.4	0.62	19.7	13
$InMo(CO)_2(exo\text{-}\eta^3\text{-}1\text{-}MeC_3H_4)$	0.144	9.1	4.0	0.11	3.0	c
$(In)_2Ti(CH_3)_2$	0.189	16.0	5.1	0.14	2.8	27
$(In)_2Zr(CH_3)_2$	0.137	1.2	3.5	0.11	4.9	27
$(In)_2Hf(CH_3)_2$	0.147	2.1	3.8	0.11	5.6	27
$[(1,3\text{-}Me_2In)_2Fe]^+$	0.169	83.1	5.7	0.08	4.4	36
	0.256	14.2	8.6	0.08	4.4	36
$(In)Cr(NO)(CO)_2$	0.125	5.7	3.8	0.11	3.5	24
$(In)Mo(CO)_3I$	0.138	79.2	4.0	0.11	9.6	26
$(In)_3UCl$	0.217	15.3	5.0	0.13	3.4	37
	0.175	34.2	4.0	0.10	2.5	37
	0.298	10.1	6.9	0.19	6.4	37
$[(In)Mo(CO)(PEt_3)(MeC_2Me)]^+$	0.125	51.9	3.5	0.07	4.8	25
$[(In)Mo(PMe_3)_2(MeC_2Me)]^+$	0.194	76.4	5.5	0.05	4.2	25
$(In)Rh\{C_6H_3(CF_3)_4C(CH_2)CH_3\}]$	0.130	1.9	3.9	0.13	5.7	38
$[(In)_2Rh_2(CO)_2(C_3H_4)]$	0.157	82.9	4.6	0.15	9.4	39
	0.267	14.4	7.8	0.18	8.8	39
$[InIr(PPh_3)_2H]^+$	0.245	3.5	7.2	0.20	5.9	c

[a] The longer M–C bonds are "trans" to CO. [b] The uncertainty for this value is large. [c] This work.

Table II. Crystallographic Data for X-ray Diffraction Studies

	$\{(C_9H_7)Ir[P(C_6H_5)_3]_2H\}BF_4\cdot CH_2Cl_2$	$(C_9H_7)Mo(CO)_2(C_4H_7)$
(A) Crystal Data		
formula	$IrP_2F_4C_{45}BH_{38}Cl_2CH_2$	$MoO_2C_{15}H_{14}$
temp, ±2 °C	24	23
space group	$P2_1/n$, No. 14	$P2_1/n$, No. 14
a, Å	12.895 (2)	11.978 (3)
b, Å	12.285 (3)	7.992 (1)
c, Å	26.566 (6)	14.109 (4)
β, deg	94.08 (2)	91.85 (3)
V, Å^3	4198 (3)	1350.1 (9)
M_r	1004.69	322.22
ρ_{calcd}, g/cm^3	1.59 (Z = 4)	1.59 (Z = 4)
(B) Measurement of Intensity Data		
radiation	Mo Kα (0.710 73 Å)	
monochromator	graphite	
detector aperture (mm)		
horizontal ($A + B \tan\theta$), A, B	3.0, 1.0	
vertical	4.0	
reflctns measd	$+h,+k,\pm l$	$+h,+k,\pm l$
max 2θ, deg	45	54
scan type	moving crystal–stationary counter	
ω scan width ($A + 0.347 \tan\theta$), deg, A =	0.90	0.90
bkgd	$^1/_4$ additional at each end of scan	
ω scan rate (variable)		
max, deg/min	10.0	10.0
min, deg/min	1.4	1.4
no. of reflctns measd	6014 with absences	3250
data used $\{F^2 \geqslant 3\,\sigma(F^2)\}$	3717	1364
(C) Treatment of Data		
abs correctn	applied	not applied
abs coeff, cm^{-1}	34.2	9.4
grid	10 × 10 × 8	
transmission coeff: max, min	0.540, 0.359	
p factor	0.02	0.03
final residuals R_1, R_2	0.046, 0.054	0.033, 0.034
esd of unit weight	2.73	1.18
largest shift/error value on final cycle	0.28	0.08
largest peak in final difference Fourier, e/Å^3	1.12	0.21

defined as σ (see Figure 6). Atwood[29] has defined another measure of the distortion, ψ, the angle slip, as the angle between the normal to the plane and the centroid–metal vector. Simple trigonometric relationships relate ψ, Δ, and the length of the centroid–metal vector.[30]

The η^5-indenyl complexes do not show a significant folding of the ring between the C(1)–C(3) and the C(1)–

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Table III. Positional and Thermal Parameters for $\{(\text{Indenyl})\text{Ir}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{H}\}\text{BF}_4\cdot\text{CH}_2\text{Cl}_2$

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*, Å^3
Ir	0.01275 (4)	0.21504 (4)	0.10441 (2)	2.812 (8)[a]
P(1)	0.1052 (2)	0.3182 (2)	0.1636 (1)	3.73 (7)[a]
P(2)	−0.0856 (2)	0.1159 (3)	0.1554 (1)	3.69 (7)[a]
C(111)	0.2215 (8)	0.2615 (9)	0.1975 (4)	3.1 (2)
C(121)	0.1674 (8)	0.4371 (9)	0.1349 (4)	2.8 (2)
C(131)	0.0238 (8)	0.3769 (9)	0.2108 (4)	3.0 (2)
C(211)	−0.0577 (8)	0.1162 (9)	0.2245 (4)	2.8 (2)
C(221)	−0.0797 (8)	−0.0321 (9)	0.1460 (4)	2.9 (2)
C(231)	−0.2250 (8)	0.1436 (9)	0.1435 (4)	2.8 (2)
C(1)	−0.0749 (9)	0.1729 (10)	0.0322 (5)	3.9 (3)
C(2)	0.0302 (10)	0.1817 (11)	0.0247 (5)	5.1 (3)
C(3)	0.0598 (9)	0.2914 (11)	0.0338 (4)	4.1 (3)
C(4)	−0.0548 (9)	0.4630 (11)	0.0512 (5)	4.6 (3)
C(5)	−0.1535 (10)	0.4939 (11)	0.0553 (5)	5.0 (3)
C(6)	−0.2354 (10)	0.4206 (11)	0.0536 (5)	4.8 (3)
C(7)	−0.2178 (10)	0.3132 (10)	0.0462 (5)	4.6 (3)
C(8)	−0.1174 (8)	0.2750 (10)	0.0412 (4)	3.7 (2)
C(9)	−0.0340 (9)	0.3511 (11)	0.0421 (5)	4.2 (3)

[a] B_{eqv} is given for atoms refined anisotropically.

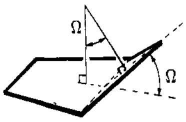

Figure 7. The fold angle, ψ, is the dihedral angle between the planes of a three-carbon and a four-carbon fragment of a five-membered ring. The three-cargon fragment includes the carbons with shortest metal–carbon bond lengths.

C(9)–C(8)–C(3) planes. A large envelope fold angle, Ω,[31] can greatly increase the value of Δ or **S**. When the Ω fold angle is large, it might be thought to be more realistic to use the C(1)–C(2)–C(3) plane as the reference plane. This generates different values, **S**′ and σ′. In our opinion, introducing still another set of parameters is not warranted. Correlations among the various previously suggested approaches and with $\overline{\Delta\text{M–C}}$[32] are better with the five-carbon reference plane. These results are summarized in Table I along with data for some analogous cyclopentadienyl complexes. The most direct comparison for the InMo(CO)$_2$(allyl) system might be expected to be the parent CpMo(CO)$_2$(allyl);[33] however, this conformation of the cyclopentadienyl ring is not comparable to that in the indenyl system and large thermal motion of the ring makes the data less reliable. The Cp complexes shown in Table I all have a Cp conformation close to that found in the indenyl.

Detailed analyses of distortions in cyclopentadienyl rings are handicapped by the accuracy of the data and the statistical uncertainties ordinarily encountered in bond lengths within the ring,[11,12,14] even in cases when large thermal motion of the ring is not a problem. Measures of envelope angle, Ω, are particularly susceptible to large deviations arising from minor variations or anomalies in carbon atom position. Slip parameters, such as Δ and ψ, involve averages over five carbon positions, which tend to make them less sensitive to small errors in position. Examination of differences in metal–carbon lengths with the $\overline{\Delta\text{M–C}}$ parameter has the advantage of the greater accuracy with which M–C distances are determined relative to C–C distances by X-ray methods.

Table IV. Selected Bond Lengths (Å) for $\{(\text{Indenyl})\text{Ir}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{H}\}\text{BF}_4\cdot\text{CH}_2\text{Cl}_2$

Ir–P(1)	2.287 (2)	C(1)–C(2)	1.39 (1)
Ir–P(2)	2.273 (2)	C(1)–C(8)	1.40 (1)
Ir–C(1)	2.216 (7)	C(2)–C(3)	1.42 (1)
Ir–C(2)	2.185 (8)	C(3)–C(9)	1.45 (1)
Ir–C(3)	2.219 (8)	C(4)–C(5)	1.34 (1)
Ir–C(8)	2.404 (7)	C(4)–C(9)	1.43 (1)
Ir–C(9)	2.400 (8)	C(5)–C(6)	1.39 (1)
P(1)–C(111)	1.831 (7)	C(6)–C(7)	1.36 (1)
P(1)–C(121)	1.855 (7)	C(7)–C(8)	1.39 (1)
P(1)–C(131)	1.840 (7)	C(8)–C(9)	1.42 (1)
P(2)–C(211)	1.845 (7)		
P(2)–C(221)	1.838 (7)		
P(2)–C(231)	1.836 (7)		

In a CpML$_3$ or CpML$_4$ complex containing the same ligands or ligands of comparable electronic character, one would expect that Δ and $\overline{\Delta\text{M–C}}$ would be nearly zero. Considering the errors normally encountered, values less than ~0.01 Å should be observed, as the electronic character of the ligands becomes different; however, consideration of the differential trans effects suggests an increase in these parameters. Thus, the difference between carbonyl and η^3-allyl ligands produces a slipping of the ring toward the allyl moiety, as evidenced by a Δ or $\overline{\Delta\text{M–C}}$ in the range of 0.04–0.10 Å. The slippage and bond lengthening is enhanced in the indenyl complexes owing to partial recovery of resonance energy in the six-membered ring upon weakening of the interaction of the metal with the C(8)–C(9) p orbitals. This effect is even greater in the [InIr(PPh$_3$)$_2$H]$^+$ complex.

As would be expected, the Δ and $\overline{\Delta\text{M–C}}$ for each compound show a strong correlation, as shown in Table I. We believe values of Δ and σ provide the best measures of slippage; however, their calculation requires some moderately involved algebraic manipulation of crystallographic

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(30) The centroid does not necessarily lie in the least-squares plane. Furthermore, in some situations it may be advantageous to use a different reference plane. Minor differences can result from the calculations if the ring is folded and the definitions are not followed rigorously.

(31) Our fold angle, Ω, is equivalent to Mingos θ + φ.[28]

(32) $\overline{\Delta\text{M–C}}$ is the difference between the average of the metal–carbon distances to C(1), C(2), and C(3) and those of C(8) and C(9). We compared **S**′ and σ, with **S** and σ for representative examples and did not find that they offer a significant advantage.

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Table V. Selected Bond Angles (deg) for $\{(\text{Indenyl})\text{Ir}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{H}\}\text{BF}_4\cdot\text{CH}_2\text{Cl}_2$

P(1)-Ir-P(2)	99.96 (7)	Ir-P(1)-C(121)	111.9 (2)	C(1)-C(2)-C(3)	107.6 (7)
P(1)-Ir-C(1)	158.8 (2)	Ir-P(1)-C(131)	113.0 (2)	C(2)-C(3)-C(9)	106.9 (7)
P(1)-Ir-C(2)	133.3 (2)	C(111)-P(1)-C(121)	98.0 (3)	C(5)-C(4)-C(9)	118.6 (8)
P(1)-Ir-C(3)	100.7 (2)	C(111)-P(1)-C(131)	107.5 (3)	C(4)-C(5)-C(6)	122.6 (8)
P(1)-Ir-C(8)	127.9 (2)	C(121)-P(1)-C(131)	104.8 (3)	C(5)-C(6)-C(7)	120.2 (8)
P(1)-Ir-C(9)	100.5 (2)	Ir-P(2)-C(211)	121.0 (2)	C(6)-C(7)-C(8)	120.5 (8)
P(2)-Ir-C(1)	96.8 (2)	Ir-P(2)-C(221)	114.8 (2)	C(1)-C(8)-C(7)	134.3 (8)
P(2)-Ir-C(2)	125.3 (2)	Ir-P(2)-C(231)	112.3 (2)	C(1)-C(8)-C(9)	106.7 (7)
P(2)-Ir-C(3)	158.0 (2)	C(211)-P(2)-C(221)	97.5 (3)	C(7)-C(8)-C(9)	118.9 (8)
P(2)-Ir-C(8)	100.9 (2)	C(211)-P(2)-C(231)	106.8 (3)	C(3)-C(9)-C(4)	133.3 (8)
P(2)-Ir-C(9)	131.4 (2)	C(221)-P(2)-C(231)	102.1 (3)	C(3)-C(9)-C(8)	107.7 (7)
Ir-P(1)-C(111)	119.7 (2)	C(2)-C(1)-C(8)	110.8 (7)	C(4)-C(9)-C(8)	119.0 (7)

Table VI. Positional and Thermal Parameters for *exo*-(Indenyl)Mo(CO)$_2$(η^3-crotyl)

atom	x/a	y/b	z/c	B_{eqv}, Å^2
Mo	0.02103 (4)	0.12314 (7)	0.26558 (3)	3.488 (9)
O(1)	0.2761 (3)	0.1298 (7)	0.3157 (3)	4.6 (1)
O(2)	0.0377 (4)	−0.1710 (6)	0.4087 (3)	6.8 (1)
C(O1)	0.1807 (5)	0.1280 (8)	0.2967 (4)	4.6 (1)
C(O2)	0.0318 (5)	−0.0621 (7)	0.3538 (4)	7.6 (1)
C(A1)	−0.0351 (5)	−0.1124 (8)	0.1792 (4)	5.4 (2)
C(A2)	0.0139 (6)	0.0057 (9)	0.1233 (4)	5.6 (2)
C(A3)	0.1232 (5)	0.0514 (9)	0.1272 (4)	4.8 (2)
C(A4)	0.1801 (6)	0.1776 (10)	0.0736 (4)	6.7 (2)
C(1)	−0.1346 (5)	0.2315 (8)	0.3398 (4)	5.0 (2)
C(2)	−0.0415 (6)	0.3246 (8)	0.3689 (4)	5.4 (2)
C(3)	0.0000 (5)	0.4120 (7)	0.2912 (4)	4.4 (1)
C(4)	−0.0778 (5)	0.4379 (7)	0.1164 (4)	4.4 (1)
C(5)	−0.1597 (5)	0.3828 (9)	0.0567 (4)	5.8 (2)
C(6)	−0.2404 (5)	0.2695 (9)	0.0849 (5)	6.1 (2)
C(7)	−0.2427 (5)	0.2097 (8)	0.1742 (5)	5.5 (2)
C(8)	−0.1580 (5)	0.2641 (7)	0.2419 (4)	4.1 (1)
C(9)	−0.0740 (4)	0.3797 (7)	0.2109 (4)	3.7 (1)

Table VII. Selected Bond Lengths (Å) for *exo*-(Indenyl)Mo(CO)$_2$(η^3-crotyl)

Mo-C(O1)	1.949 (7)	Mo-C(1)	2.335 (6)
Mo-C(O2)	1.936 (6)	Mo-C(2)	2.313 (6)
Mo-C(A1)	2.330 (6)	Mo-C(3)	2.352 (5)
Mo-C(A2)	2.215 (6)	Mo-C(9)	2.457 (6)
Mo-C(A3)	2.407 (6)	Mo-C(8)	2.436 (6)
C(O1)-O(1)	1.165 (6)	C(1)-C(8)	1.424 (8)
C(O2)-O(2)	1.166 (6)	C(2)-C(3)	1.405 (8)
C(A1)-C(A2)	1.373 (8)	C(3)-C(9)	1.439 (7)
C(A2)-C(A1)	1.373 (8)	C(4)-C(9)	1.412 (7)
C(A2)-C(A3)	1.359 (8)	C(4)-C(5)	1.345 (8)
C(A3)-C(A2)	1.359 (8)	C(5)-C(6)	1.392 (9)
C(A3)-C(A4)	1.444 (9)	C(6)-C(7)	1.349 (8)
C(A4)-C(A3)	1.444 (9)	C(7)-C(8)	1.438 (8)
C(1)-C(2)	1.391 (8)	C(8)-C(9)	1.444 (8)

data presented in published structures. Fortunately, the close correlation of the magnitude of $\overline{\Delta\text{M–C}}$ with Δ suggests that Δ provides a somewhat less exact but more conveniently obtained, measure of slippage.

Consideration of σ values illustrates one feature of these slipped η^5-indenyl complexes which allows fairly reliable predictions; that is, the predominent conformation will have the six-membered ring trans to the ligand or ligands with the greatest trans effect.

Comparison of the parameters for the entries in Table I shows that the cyclopentadienyls and the indenyls investigated fall into two categories. Most have slip distortions ($\alpha < 0.3$) which are small enough so that the cyclopentadienyl or indenyl may be considered essentially as a η^5 ligand. In contrast, for the case of $\text{Cp}_2\text{W(CO)}_2$, one Cp has a slip distortion which is so great ($\Delta = 0.93$) that the Cp is unequivocally η^3. No intermediate case appears to have yet been reported.

Experimental Section

The preparation of the molybdenum complex is described elsewhere.[22] The $[(\eta^5\text{-indenyl})\text{Ir}\{\text{P}(\text{C}_6\text{H}_5)_3\}_2\text{H}]\text{BF}_4$ complex was formed in the reaction of indene and $[\text{IrH}_2(\text{Me}_2\text{CO})_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]\text{BF}_4$ at 150 °C.[40] NMR spectra were obtained on Bruker 250- and 500-MHz NMR spectrometers.

Crystallographic Analyses. Crystals suitable for diffraction analysis were obtained from dichloromethane–hexane solutions by cooling to −10 °C. The crystals were mounted in thin-walled glass capillaries. Diffraction measurements were carried out on an Enraf-Nonius CAD-4 fully automated four circle diffractometer. Unit cells were determined and refined from 25 randomly selected reflections obtained by using the CAD-4 automatic search, center, index, and least-squares routines. The crystal data and the data collection parameters are listed in Table II. Data processing was performed on Digital PDP 11/45 and 11/23 computers using the Enraf-Nonius SDP program library (Version 18). Absorption corrections were not performed on the molybdenum compound owing to the low absorption coefficients. Neutral atom scattering factors were calculated by standard procedures.[41a] Anomalous dispersion corrections were applied to all atoms.[41b] Full-matrix least-squares refinements minimized the function $\sum_{hkl} w(F_o - F_c)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{\text{raw}})^2 + (pF_o^2)^2]^{1/2}/Lp$.

The space group $P2_1/n$ for both complexes was established by the systematic absences. The structures were solved by a combination of Patterson and difference Fourier techniques.

For the molybdenum complex, anisotropic refinement of all non-hydrogen atoms was carried out. Idealized hydrogen atom positions were then calculated and included in the final refinement stages but were not refined themselves. Calculated hydrogen atom positions were also used in the iridium structure. Owing to the large number of atoms, only the iridium and two phosphorus atoms were refined anisotropically. These refinements converged to the residuals and parameters given in Table II. The values of the fractional coordinates are listed in Tables III and VI. The bond lengths and angles and the esds obtained from the inverse matrix obtained on the final cycle of refinement for each compound are given in Tables IV, V, VII, and VIII. Tables of

Table VIII. Selected Bond Angles (deg) for (Indenyl)Mo(CO)$_2$(η^3-crotyl)

C(O1)-Mo-C(O2)	80.0 (3)	Mo-C(O2)-O(2)	178.4 (5)	C(5)-C(6)-C(7)	122.2 (6)
C(O1)-Mo-C(A1)	113.5 (3)	C(A1)-C(A2)-C(A3)	126.2 (7)	C(6)-C(7)-C(8)	118.6 (6)
C(O1)-Mo-C(A2)	102.8 (3)	C(A2)-C(A3)-C(A4)	129.6 (7)	C(1)-C(8)-C(9)	107.1 (6)
C(O1)-Mo-C(A3)	70.5 (2)	C(2)-C(1)-C(8)	108.6 (6)	C(1)-C(8)-C(7)	134.5 (6)
C(O2)-Mo-C(A1)	74.4 (3)	C(1)-C(2)-C(3)	109.6 (5)	C(9)-C(8)-C(7)	118.4 (5)
C(O2)-Mo-C(A2)	105.0 (3)	C(2)-C(3)-C(9)	107.5 (5)	C(3)-C(9)-C(4)	133.2 (6)
C(O2)-Mo-C(A3)	108.3 (3)	C(9)-C(4)-C(5)	118.9 (6)	C(3)-C(9)-C(8)	107.1 (5)
Mo-C(O1)-O(1)	179.5 (6)	C(4)-C(5)-C(6)	122.2 (6)	C(4)-C(9)-C(8)	119.7 (6)

anisotropic thermal parameters, structure factor amplitudes, and calculated hydrogen atom positions, phenyl carbon positions, etc. are available for both structures in the supplementary material.

Registry No. $CpMo(CO)_2$(*endo*-η^3-2-MeC_3H_4), 95781-86-5; $CpMo(CO)_2$(*exo*-η^3-C_6H_9), 84117-08-8; $CpMo(CO)_2$(*exo*-η^3-C_7H_{11}), 84117-12-4; (η^5-Cp)$W(CO)_2$(η^3-Cp), 65862-57-9; $InMo(CO)_2$(*exo*-η^3-1-MeC_3H_4), 95781-87-6; $(In)_2Ti(CH_3)_2$, 49596-02-3; $(In)_2Zr(CH_3)_2$, 49596-04-5; $(In)_2HF(CH_3)_2$, 49596-06-7; $[(1,3\text{-}Me_2In)_2Fe]^+$, 56285-02-0; $(In)Cr(NO)(CO)_2$, 60260-19-7; $(In)Mo(CO)_3I$, 31870-77-6; $(In)_3UCl$, 11082-70-5; $[(In)Mo(CO)PEt_3)(MeC_2Me)]^+$, 78090-93-4; $[(In)Mo(PMe_3)_2(MeC_2Me)]^+$, 78091-05-1; $[(In)Rh\{C_6H_3(CF_3)_4C(CH_2)CH_3\}]$, 63428-47-7; $[(In)_2Rh_2(CO)_2(C_3H_4)]$, 81249-02-7; $[InIr(PPh_3)_2H]BF_4$, 95616-25-4; $\{(C_9H_7)Ir[P(C_6H_5)_3]_2H\}BF_4 \cdot CH_2Cl_2$, 95616-26-5.

Supplementary Material Available: Tables of anisotropic thermal parameters, structure factor amplitudes, and calculated hydrogen atom positions, phenyl carbon positions, etc. for both structures (21 pages). Ordering information is given on any current masthead page.

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(41) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1975; Vol. IV: (a) Table 2.3.1, pp 146–50; (b) Table 2.2B, pp 99–101.

(42) We wish to acknowledge the National Science Foundation for financial support and Johnson Matthey for a loan of iridium. We also wish to thank the National Science Foundation for support of the NSF Northeast Regional NMR Facility.

Communications

Hydrido Heterobimetallic Bis(diphenylphosphino)methane-Bridged Ru–Rh Complexes. Activation of a P–C Bond of Bis(diphenylphosphino)methane To Give a Heterobimetallic Ru–Rh Complex Containing a *trans*-Hydridophenylruthenium Moiety. X-ray Crystal Structure of $RuRhH(C_6H_5)(C_8H_{12})[C_6H_5PCH_2(C_6H_5)_2]$-$[(C_6H_5)_2PCH_2P(C_6H_5)_2] \cdot 0.5C_6H_5CH_3$

Béatrice Delavaux, Bruno Chaudret, Francoise Dahan, and René Poilblanc*

Laboratoire de Chimie de Coordination du CNRS associé à l'Université Paul Sabatier, 31400 Toulouse, France

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Summary: $RuH_2(dppm)_2$ (dppm = bis(diphenylphosphino)methane) reacts with $[RhCl(COD)]_2$ (COD = cyclooctadiene) in toluene to give quantitatively $RuRhH_2Cl(COD)(dppm)_2$ (**1**), a heterobimetallic complex shown to contain a single bridging dppm ligand as well as one bridging hydride and one bridging chloride group. The same reaction occurs with $[IrCl(COD)]_2$ but in this case some redistribution to $RuHCl(dppm)_2$ is also observed. **1** does not react with ethylene but decomposes slowly under H_2; it reacts with CO to give the bis dppm-bridged complex $RuRhCl(CO)_3(dppm)_2$ (**4**) and with $P(OMe)_3$ to give $RhH[P(OMe)_3]_4$ and $RuHCl[P(OMe)_3](dppm)_2$ (**5**) which contains a monodentate dppm group. Finally, with CH_3Li a quantitative yield of $RuRhH(C_6H_5)(C_8H_{12})[C_6H_5PCH_2P(C_6H_5)_2][(C_6H_5)_2PCH_2P(C_6H_5)_2]$ (**6**) is obtained. This complex is shown to contain a bridging phosphido group and a *trans*-hydridophenylruthenium moiety.

Introduction

Preparation and reactivity of heterobimetallic complexes are a largely studied subject, but most of the research has been oriented so far toward CO reduction.[1] Many such species containing dppm as bridging ligand have been prepared recently, mostly by Shaw et al.[2] As part of our interest in hydride complexes as possible precursors for C–H activation reactions,[3] we developed a method for the preparation of ruthenium-containing hydrido bimetallic compounds using the chelated complex $RuH_2(dppm)_2$ (dppm = bis(diphenylphosphino)methane).[4] We have recently shown that this bis dppm-bridged complexes could be obtained from the reaction of $RuH_2(dppm)_2$ or $Ru(COD)(dppm)_2$ (COD = cyclooctadiene) with $[RhCl(CO)_2]_2$.[5] In this paper we describe the reaction of $RuH_2(dppm)_2$ with the analogous carbonyl-free complex $[RhCl(COD)]_2$ and the activation of a P–C bond of dppm to give a bimetallic Ru–Rh complex containing a *trans*-hydridophenylruthenium moiety.

$RuH_2(dppm)_2$ reacted smoothly at room temperature in toluene with $[RhCl(COD)]_2$ to give a quantitative yield of a bright orange compound analyzing for $RuRhH_2Cl(COD)(dppm)_2$ (1).[6] This air-stable complex is very soluble in common organic solvents except alkanes. A terminal hydride on ruthenium as well as a bridging one are observed by ^1H NMR spectroscopy whereas the ^{31}P NMR spectrum shows four different phosphorus atoms, two of which are coupled to rhodium ($J_{Rh\text{-}P_2}$ = 130 Hz; $J_{Rh\text{-}P_3}$ = 5 Hz). The spectrum is first order and is attributed unambiguously. 1 simply results from the association between $RuH_2(dppm)_2$, after opening of one chelated dppm group, with a "RhCl(COD)" moiety. The presence of one bridging hydride and one bridging chloride is deduced from

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(6) Selected spectroscopic data for 1 (all NMR spectra were recorded on a Bruker WH90 or WH250 spectrometer operating in the Fourier transform mode. Chemical shifts are relative to Me_4Si (^1H and ^{13}C NMR) or external H_3PO_4 in D_2O (^{31}P NMR): IR ν(Ru–H) 1990 cm^{-1}; ^1H NMR (in C_6D_6) $\delta(H_1)$ −14.6 (q, $J_{P\text{-}H}$ = 21 Hz), $\delta(H_2)$ −15.6 ($J_{Rh\text{-}H}$ = 22 Hz), $\delta(CH_2)$ 4.6 (1), 4.1 (2), 2.5 (1); ^{31}P NMR (in C_6D_6/C_7H_8) $\delta(P_1)$ 45.7 (ddd), $\delta(P_2)$ 22.5 (dddd), $\delta(P_3$ 14.1 (ddt), $\delta(P_4)$ 7.1 (ddd), $J_{P_1P_2}$ = 84 H, $J_{P_1P_3}$ = 29.5 Hz, $J_{P_1P_4}$ = 313 Hz, $J_{P_3P_4}$ = 68 Hz, $J_{P_2P_3}$ = 5 Hz, $J_{P_2P_4}$ = 12 Hz, J_{P_2Rh} = 134 Hz, J_{P_3Rh} = 3 Hz; ^{13}C NMR in (C_7D_8) $\delta(CH_2(dppm))$ 30.4, 62.1, δ(CH(COD)) 75.9, δ(CH(COD)) 36.9, 28.5. Anal. Calcd for $RuRhC_{58}ClH_{38}P_4$: C, 62.3; H, 5.29; Cl, 3.2; P, 11.1. Found: C, 62.2; H, 5.2; Cl, 3.0; P, 11.0.

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