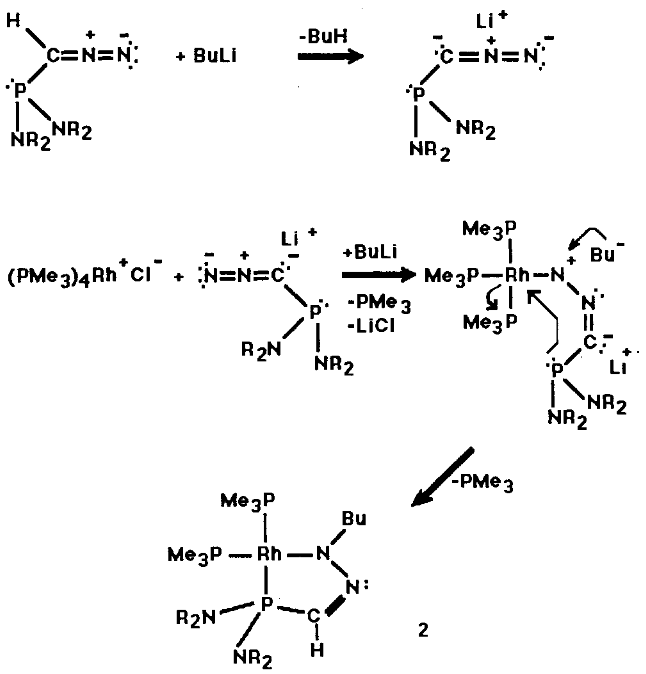
Scheme I



P1,C13,N3,N4. This ring is planar[11] with bond distances intermediate between single and double bonds, which confirms electron delocalization.

The mechanism of the reaction leading to 2 is of obvious interest since it is unprecedented. A possibility is that the diazo precursor reacts through the N terminus, affording a transient nitrile imine intermediate which is stabilized as an pyrazolyne heterocycle by reaction with butyllithium and by ring formation through the phosphorus lone pair. (This is in good agreement with the increase of the yield when a twofold excess of BuLi is used (Scheme I).) Such a reactivity is also observed when $LiC(N_2)P(N\text{-}i\text{-}Pr_2)_2$ reacts with organic electrophiles, the reaction occurring either at carbon, leading to diazo derivatives, or at the terminal nitrogen, affording nitrile imine derivatives.[12]

In conclusion, the difference in reactivity observed between these two diazo anions, i.e. $[C(N_2)[(S{=})P(N\text{-}i\text{-}Pr_2)_2]^-$ and $[C(N_2)[P(N\text{-}i\text{-}Pr_2)_2]^-$, illustrates the influence of the diazo substituent on the bonding. The electron-attracting $(S{=})P(N\text{-}i\text{-}Pr_2)_2$ group increases the negative charge at the α-carbon, thus giving rise to a C-bonded diazo derivative, while $[P(N\text{-}i\text{-}Pr_2)_2]$ bearing an electron pair on the phosphorus atom leaves more negative charge at the γ-nitrogen, thus giving rise to the N-coordinated compound. Further experiments are under active investigation in order to confirm the mechanism of these reactions and to study the reactivity of these new carbyne or carbene precursors.

Supplementary Material Available: Crystal data and details of data collection and structure refinement (Table I), fractional atomic coordinates with estimated standard deviations in parentheses (Table II), final anisotropic thermal parameters ($Å^2 \times 100$) with estimated standard deviations in parentheses (Table III), and hydrogen atomic positional and thermal parameters (Table IV) (4 pages); observed and calculated structure factor amplitudes (Tables V) (18 pages). Ordering information is given on any current masthead page.

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(11) The equation of the least-squares plane through Rh,-P1,C13,N3,N4 is $3.0654X - 8.9240Y + 2.1705Z + 5.0778 = 0$. Distances of these atoms from the plane are 0.0138 (Rh), –0.0317 (P1), 0.0066 (N4), –0.0392 (N3), and 0.0506 (C13).

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Interaction between a Vinylcarbene Complex and a Phosphole Ring: Synthesis of a New *cis*-[(7-Phosphanorbornenyl)ethoxycarbene]tetracarbonylchromium Complex

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Summary: The one-step synthesis of a new (phosphinocarbene)tetracarbonylchromium chelate is performed via an intramolecular [4 + 2] cycloaddition between a phosphole and a vinylcarbene complex.

Recently, we published some applications of the Fischer carbene complexes in the synthesis of new low-coordinated phosphorus compounds via their coupling with phosphinidene complexes.[1]

In view of the synthetic potential of these carbene complexes in the phosphorus field, we decided to explore some other types of reactions. In this paper, we take advantage of the dienophilicity of vinylcarbene complexes to build some new types of phosphinocarbene chelates.

Since the $M(CO)_5$ groups (M = Cr, Mo, W) are isolobal with the oxygen atom,[2] vinylcarbene complexes may be regarded as analogues of acrylic esters and thus can react as the 2π component in [2 + 4] cycloadditions with some dienes.[3] However, as far as we know, no intramolecular Diels–Alder reaction of this type has been described probably because it is not so obvious to keep a free and reactive dienic system close to the coordination sphere of a metal. We report here the easy introduction of a phosphole ring into the coordination sphere of a vinylcarbene chromium complex. The cis disposition of the two ligands allows a [4 + 2] intramolecular cycloaddition to take place between the phosphole dienic system and the C=C double bond of the carbene. A new cis-[(7-phosphanorbornenyl)ethoxycarbene]tetracarbonylchromium complex is thus obtained in one step.

The reaction of the carbene complex 1[4] with a slight excess of the 1-phenyl-3,4-dimethylphosphole (2)[5] in hexane at 60 °C for 6 h afforded directly complex 3[6] in ca. 85% yield (Scheme I).

Compound 3 was fully characterized by elemental analysis and mass spectrometry (EI, 70 eV): m/z (relative intensity) 512 (M^+, 10), 484 ($M^+ - CO$), 456 ($M^+ - 2CO$),

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(6) Compound 3 was purified by chromatography on silica gel (eluent pentane/CH_2Cl_2, 3/1): salmon crystals; mp 128 °C (with decomposition); ^{31}P NMR ($CDCl_3$) δ_p + 168.1 (reference external 85% H_3PO_4, δ positive for downfield shifts); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ_C 14.99 (s, Me), 15.98 (s, Me), 51.58 (d, $^1J_{C-P}$ = 20.7 Hz, CH), 56.39 (d, J_{C-P} = 16.6 Hz, CH), 61.51 (d, J_{C-P} = 23.8 Hz, CH), 66.38 (d, J_{C-P} = 26.7 Hz, CH), 76.47 (s, OCH_2), 140.98 (d, $^2J_{C-P}$ = 9.6 Hz, C=C), 219.80 (d, $^2J_{C-P}$ = 12 Hz, CO), 221.48 (d, $^2J_{C-P}$ = 13.5 Hz, CO), 229.77 (s, CO), 231.93 (d, $^2J_{C-P}$ = 12 Hz, CO), 356.36 (d, $^2J_{C-P}$ = 7.8 Hz, C=Cr); ^1H NMR ($CDCl_3$) δ 0.94 (s, CH_3), 1.59 (t, CH_3), 1.68 (s, CH_3), 3.07 (m, 2 H, PC_1H), 3.63 (m, 1 H, C_6HPh), 3.97 (m, 1 H, $C_5HC{=}Cr$), 5.03 (q, 2 H, OCH_2); IR (hexane) ν_{CO} 2010 m, 1940 m, 1910 vs, 1895 s cm^{-1}. Anal. Calcd for $C_{27}H_{25}O_5PCr$: C, 63.28; H, 4.88. Found: C, 63.20; H, 5.19.

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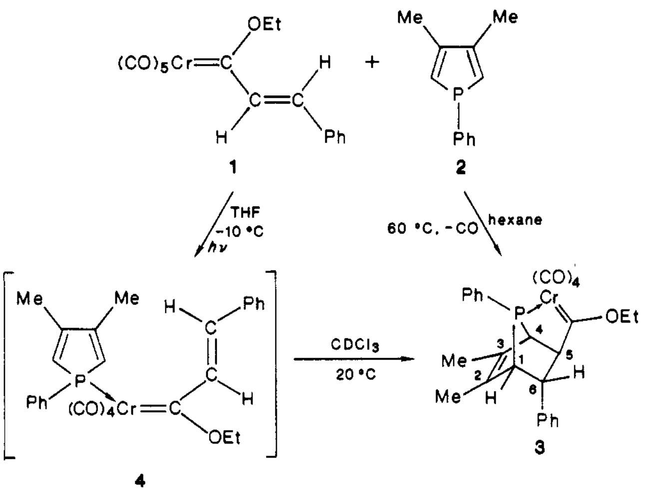
Scheme I



428 (M$^+$ − 3CO), 400 (M$^+$ − 4CO, 100). Its IR spectrum indicated a tetracarbonylchromium structure. Its ^{1}H and ^{13}C NMR spectra[6] confirmed the proposed formulation. The stereochemistry at C$_6$ was established on the basis of the ^{1}H NMR spectrum. Decoupling experiments showed a weak $^3J(H–C_1–C_6–H)$ coupling (ca. 1–2 Hz) which implies that H–(C$_6$) occupies the exo position. Thus, as expected, the Diels–Alder reaction takes place with retention of the stereochemistry at the C=C double bond of the dienophile. The first step of this reaction is the displacement by the λ^3-phosphorus of one cis CO on the chromium atom leading to the *cis*(vinyl ethoxycarbene)(1-phenyl-3,4-dimethylphosphole)tetracarbonylchromium complex 4 (Scheme I). Indeed, it proved possible to detect this intermediate compound 4 after its photochemical generation at −10 °C, in THF by irradiation with a TQ 150 Hanau medium-pressure lamp with a Pyrex filter. Under such conditions, the phosphole behaved as a classical phosphorus ligand toward a carbene complex.[7] This was also suggested by the following experiment. When we heated the [(phenylethoxy)carbene]pentacarbonyltungsten with a slight excess of phosphole 2 in hexane at 60 °C for 6 h we isolated the *cis*-(phosphole)(ethoxycarbene)tetracarbonyltungsten[8] in ca. 90% yield. Complex 4 is deep purple: its ^{31}P NMR spectrum displayed a single peak at 52 ppm (in THF). However, when we tried to record its ^{1}H NMR spectrum in CDCl$_3$, decomposition took place to give 3. This fact was confirmed by the ^{31}P NMR spectrum of the same sample which showed the presence of two peaks at 168 and 50.7 ppm (CDCl$_3$) and by the ^{13}C NMR spectrum which showed two carbenic carbon signals and the appearance of a phosphanorbornenyl system.[9]

It is interesting to note here that somewhat related intramolecular [4 + 2] cycloadditions between phosphole dienic systems and C=C double bonds within a single coordination sphere have already been described.[10]

We are currently exploring the possibilities offered by this approach as well as the reactivity of this new type of complex.

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(9) 4 → 3: ^{31}P NMR (CDCl$_3$) δ_P 168.0 (3) and 50.7 (4); ^{13}C NMR (CDCl$_3$) δ_C 14.9, 15.3, 15.9, 17.2, 17.4 (Me), 51, 56, 61, 66 (CH and OCH$_2$ of 3), 334.2 (C=Cr of 4), 356.3 (C=Cr of 3).

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Sequential Insertion of CO into Rhodium–Nitrogen μ-Imido/Amido Bonds: Formation of Isocyanate and Dimetallocycloimide Complexes[1]

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Summary: Treating Rh$_2$(μ-NHMe)(CO)$_2$(μ-dppm-H)(μ-dppm) (dppm-H = bis(diphenylphosphino)methanide; dppm = bis(diphenylphosphino)methane) or tautomeric mixtures of Rh$_2$(μ-NHR)(CO)$_2$(μ-dppm-H)(μ-dppm) and Rh$_2$(μ-NR)(CO)$_2$(μ-dppm)$_2$ (R = *p*-MePh or Ph) with 1 equiv of CO gives Rh$_2$(μ-η^2-RNCO)(CO)$_2$(μ-dppm)$_2$ (R = Me, *p*-MePh, or Ph). With excess CO Rh$_2$(μ-CO)(CO)$_2$(dppm)$_2$, RNCO, and (RHN)$_2$CO are obtained for R = *p*-MePh or Ph. With R = Me, Rh$_2$[μ-η^2-C(O)N(Me)C(O)](μ-CO)(CO)$_2$(dppm)$_2$ and Rh$_2$(μ-CO)(CO)$_2$(dppm)$_2$ are obtained.

Catalytic carbonylations of organoazides and nitroaryls are frequently postulated to proceed via metal imido intermediates.[2] In support of this proposal imido complexes have been isolated from reactions of metal complexes with organoazides, nitroaryls, and nitrosoaryls.[3] In the catalytic processes the formation of nitrogen–carbon bonds is a key step. In most cases, isocyanate (formed by coupling of the imido ligand and CO) is the final product or is a probable precursor to the final product. However, until recently[3a] the isolated imido complexes have given little, if any, isocyanates or products derived from isocyanates when treated with CO under mild conditions.[4] This communication reports the facile formation of isocyanate and dimetallocycloimide complexes and free isocyanates and ureas by the formal single and double insertion of CO into the metal–nitrogen bonds of rhodium μ-imido/amido A-frame complexes.

Previously we reported the preparation and characterization of Rh$_2$(μ-NHR)(CO)$_2$(μ-dppm-H)(μ-dppm) (**1**, R = Me, dppm-H = bis(diphenylphosphino)methanide, dppm = bis(diphenylphosphino)methane) and tautomeric mixtures of 1 and Rh$_2$(μ-NR)(CO)$_2$(μ-dppm)$_2$ (**2**, R = *p*-MePh or Ph).[5] When solutions (CH$_2$Cl$_2$, toluene or benzene) of

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(1) Part 3 in a series entitled *Late Transition Metal μ-Oxo and μ-Imido Complexes*. For part 2 see ref 5.

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