Chemistry of the organochromium(I) radical CpCr(CO)3.bul.. X-ray structure of a stable derivative, CpCr(CO)2(PPh3).bul.

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Organometallics, **1986**, 5 (12), 2563-2565• DOI: 10.1021/om00143a032 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

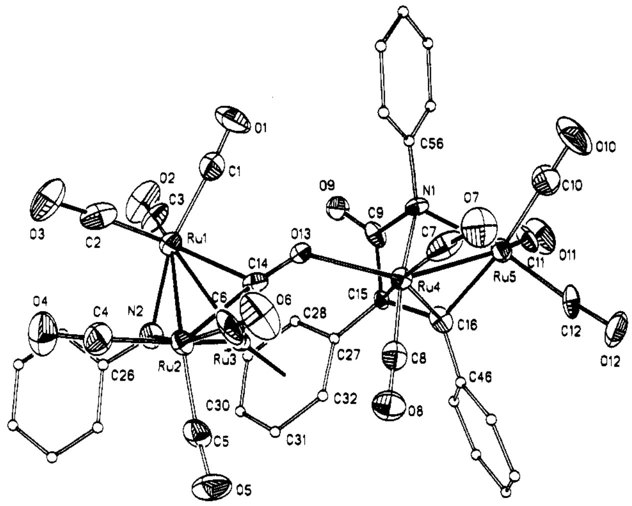

Figure 2. Molecular structure and labeling scheme for **4** (40% thermal ellipsoids). Only one of the chemically indistinguishable but independent molecules in the asymmetric unit is shown. Bond distances (Å) bond angles (deg): Ru(1)–C(14), 2.18 (1); Ru(2)–C(14), 2.21 (1); Ru(3)–C(14), 1.98 (1); ⟨av⟩ Ru(3)–C(η^6-C_6H_5), 2.27 (2); C(14)–O(13), 1.27 (2); O(13)–Ru(4); 2.23 (1); ⟨av⟩ Ru–C(14)–Ru, 79.7 (6); Ru(4)–O(13)–C(14), 128 (1).

demonstration of such chemistry from a binuclear metallapyrrolidone complex.

It is interesting to compare the chemistry described herein to the recently reported reactions of alkynes with the μ_3-phosphinidene iron analogue of **1**, $Fe_3(\mu_3\text{-}PC_6H_4OCH_3)(CO)_{10}$.[22] These reactions gave trinuclear products from either substitution of alkyne for a cluster CO (photolysis) or insertion of the alkyne into an Fe–P bond (thermolysis). In contrast to the results reported herein, no coupling of the phosphinidene ligand with CO was observed, further illustrating the significant reactivity differences between isoelectronic μ_3-nitrene and μ_3-phosphinidene ligands.[4]

It is clear from this and related studies that μ_3-nitrene ligands in metal clusters can combine with a variety of other ligands including hydrides,[3f,g] carbenes,[4] acyls,[5] methoxycarbonyls,[5] and now alkynes. The further reactivity of this ligand is under exploration in our laboratory, with current efforts directed toward its reactions with olefins and other unsaturated organic substrates.

Acknowledgment. We thank the National Science Foundation for support of this research and for contributing funds toward the purchase of the X-ray diffractometer at the University of Delaware. Dr. G. Steinmetz and R. J. Hale at the Tenessee Eastman Company are acknowledged for obtaining mass spectra.

Registry No. **1**, 51185-99-0; **2**, 105121-10-6; **3**, 105102-79-2; **4**, 105121-11-7; **5**, 33310-08-6; PhC≡CMe, 673-32-5; PhC≡CPh, 501-65-5; $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$, 51233-18-2; $Ru_3(CO)_{12}$, 15243-33-1; Ru, 7440-18-8.

Supplementary Material Available: Tables of atomic positional parameters, anisotropic thermal parameters, bond lengths and angles, and calculated hydrogen atom positions for **2** and **4** (15 pages); listings of structure factors for **2** and **4** (61 pages). Ordering information is given on any current masthead page.

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Chemistry of the Organochromium(I) Radical $CpCr(CO)_3\cdot$. X-ray Structure of a Stable Derivative, $CpCr(CO)_2(PPh_3)\cdot$

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Received August 12, 1986

Summary: The metal-metal-bonded dimer $[CpCr(CO)_3]_2$ (II) reacts (a) with Bu_3SnH to give $CpCr(CO)_3H$ and $CpCr(CO)_3SnBu_3$ and (b) with methyl iodide to give $CpCr(CO)_3I$ and $CpCr(CO)_3Me$. Both reactions appear to involve the chromium-centered radical $CpCr(CO)_3\cdot$, formed spontaneously via dissociation of II. The X-ray crystal structure of the chromium-centered radical $CpCr(CO)_2(PPh_3)\cdot$ has been determined; the compound is isostructural with the 18-electron species $CpMn(CO)_2(PPh_3)$ but exhibits a deformation which may be attributed to the electron "hole".

We have recently reported a mechanistic investigation, involving CIDNP studies, of the hydrometalation ("insertion") and hydrogen-transfer reactions of $HMn(CO)_5$ and $CpFe(CO)_2H$ with conjugated dienes.[1] In an attempt to extend this work to similar reactions of the hydride $CpCr(CO)_3H$[2] (I), we have observed no CIDNP polarizations but did to our surprise observe coalescence of the cyclopentadienyl ^1H NMR resonance of I with that of the reaction byproduct $[CpCr(CO)_3]_2$ (II). Although we can offer for this behavior no obvious rationalization involving direct exchange between I and II, the chromium–chromium bond of the latter is sufficiently weak[3] that II dissociates slightly in solution to form the paramagnetic monomer $CpCr(CO)_3\cdot$ (III).[4] Thus one may postulate direct hydrogen atom exchange between I and III, i.e.

$$[Cr]H + [Cr] \rightarrow [Cr]\cdots H\cdots[Cr] \rightarrow [Cr] + H[Cr] \quad (1)$$

$$[Cr] = CpCr(CO)_3$$

Precedent for this reaction is found in the facile transfer of hydrogen from $CpMo(CO)_3H$ to photogenerated $CpW(CO)_3\cdot$,[5] and indeed, atom abstraction reactions are a characteristic process of transition-metal-centered radicals such as III.[6] In the system under consideration here,

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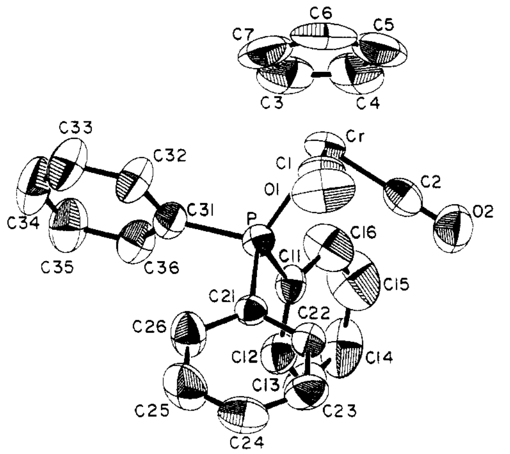

Figure 1. The molecular structure of $CpCr(CO)_2PPh_3\cdot$, showing the atom numbering scheme. Selected bond lengths (Å) and angles (deg): Cr–P = 2.345 (1), $Cr–C_1$ = 1.826 (3), $Cr–C_2$ = 1.816 (4), $C_1–O_1$ = 1.16 (12), $C_2–O_2$ = 1.16 (12), $P–Cr–C_1$ = 93.3 (1), $P–Cr–C_2$ = 93.4 (1), $C_1–Cr–C_2$ = 80.9 (1).

dissociation of II must be facile, leading to the possibility that the chemistry of II might generally reflect the reactivity of III. There is currently much interest in the properties of 17-electron, metal-centered radicals such as III, usually generated photochemically,[6] and a novel opportunity to study thermally generated metal-centered radicals seemed to be presented. We therefore report here preliminary results of an investigation into the chemistry of II with substrates which are known to react readily with metal-centered radicals.[6]

Reactions of II with tributyltin hydride in tetrahydrofuran and toluene in the dark proceed as in (2). The

$$\text{II} + 2Bu_3SnH \rightarrow \text{I} + CpCr(CO)_3SnBu_3 \qquad (2)$$

reactions proceed quantitatively (by NMR and IR spectroscopy) within 5 min at room temperature, although the product I also reacts slowly with excess Bu_3SnH to form more of the chromium–tin compound. In contrast the analogous molybdenum dimer $[CpMo(CO)_3]_2$ is reported to react thermally with Me_3SnH at a negligible rate to form a very small yield of $CpMo(CO)_3SnMe_3$,[7] while the same molybdenum dimer and its tungsten analogue react photochemically with Bu_3SnH to form the corresponding tin–molybdenum and –tungsten compounds *plus hydrogen*[6f] (eq 3). The much higher thermal reactivity of the

$$[CpM(CO)_3]_2 + 2Bu_3SnH \rightarrow 2CpM(CO)_3SnBu_3 + H_2 \qquad (3)$$

$$M = Mo, W$$

chromium dimer II seems best rationalized on the basis of the lower metal–metal bond strength of that compound relative to its heavier analogues,[8] which are not in equilibrium with significant amounts of monomers. Thus a reasonable intermediate would be one in which III and Bu_3SnH form a hydrogen atom bridged species analogous to that shown in (1), a route not available thermally to the molybdenum and tungsten compounds. The contrast in reaction products in (2) and (3) is also of interest and strongly suggests that the two reactions proceed via different mechanisms. The chemistry represented by (3) was induced via photolysis of the molybdenum and tungsten dimers in the presence of the tin hydride and is believed to involve oxidative addition of the tin–hydrogen moiety to the metal radicals rather than a direct hydrogen–metal interaction as in (1). Thus the differences in behavior may arise because of photochemical activation of the molybdenum and tungsten radicals toward oxidative addition, either because of ligand loss or because of the lowered ionization potential of an excited state species. It certainly seems likely, on the basis of relative metal–hydrogen bond strengths,[8] that the molybdenum and tungsten monomers should be able to abstract a hydrogen atom from Bu_3SnH more readily than does III. We note also that substituted manganese (0) radicals of the type $Mn(CO)_3L_2$ (L = tertiary phosphine) abstract the hydrogen atom from Bu_3SnH, although subsequent coupling of manganese and tin radicals is subject to severe steric hindrance.[6g]

Compound II also reacts in tetrahydrofuran with alkyl halides and trialkytin halides as in (4) and (5), atom

$$\text{II} + MeI \rightarrow CpCr(CO)_3Me + [CpCr(CO)_3(THF)]I \qquad (4)$$

$$\text{II} + R_3SnX \rightarrow CpCr(CO)_3SnR_3 + [CpCr(CO)_3(THF)]X \qquad (5)$$

transfer reactions of a type generally characteristic of metal-centered radicals.[6] Although the solvate complexes have not previously been characterized, they were identified by their IR spectra[9] and by their facile, reversible conversion to the known halo complexes $CpCr(CO)_3X$ (X = Br, I)[11] on removal of the solvent. It is interesting to note that coupling of the alkyl and chromium radicals to give $CpCr(CO)_3Me$ is facile; this type of product has been anticipated in photochemical reactions of metal–metal bonded compounds with alkyl halides but is rarely observed because of low concentrations of metal radicals.[6c]

Finally, we note that metal-centered radicals are generally stabilized with respect to dimerization by substitution of carbon monoxide by bulky ligands. Thus radicals of the type $M(CO)_4L\cdot$ (M = Mn, Re) become more persistent as L becomes more sterically demanding,[6e] and $[CpCr(CO)_2\{P(OMe)_3\}]_2$, although a diamagnetic dimer in the solid state, is much more extensively dissociated in solution than is II.[4c] In an attempt to prepare a persistent chromium radical for study, we have therefore reacted II with the relatively bulky triphenylphosphine, obtaining in quantitative yield yellow crystals of $CpCr(CO)_2PPh_3\cdot$ (IV). Compound IV has been prepared previously and characterized by elemental analysis[10] but was apparently assumed to be dimeric and was not studied in detail. We find, however, that IV has a magnetic moment corresponding to one unpaired electron in the solid state and exhibits a ^1H NMR spectrum containing only very broad resonances. The IR spectrum of IV exhibits two ν_{CO} at 1920 and 1805 cm^{-1}, as compared with 1932 (s), 1867 (s), and 1855 (m, sh) cm^{-1} for $CpCr(CO)_2(PPh_3)H$,[12] which is formed by treating IV with hydrogen gas.

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(12) The ^1H NMR spectrum of the hydride in benzene-d_6 exhibits a hydride resonance at δ −5.21 (J_{PH} = 80 Hz), a Cp resonance at δ 4.22 (J_{PH} = 1.2 Hz), and a broad phenyl multiplet at δ ~7.2.

The crystal structure of IV has been determined,[13] and the geometry is shown in Figure 1, where the monomeric nature (the shortest Cr–Cr distance is 6.29 Å) and the "three-legged piano stool" geometry are apparent. The compound is isostructural with $CpMn(CO)_2(PPh_3)$[19] (V) but exhibits interesting, subtle differences in structure. Thus while V exhibits normal OC–Mn–CO and P–Mn–CO bond angles of 92.42 (41)° and 92.65 (27)° or 90.52 (32)°, respectively, IV exhibits OC–Cr–CO and P–Cr–CO bond angles of 80.9 (1)° and 93.3 (1)° or 93.4 (1)°, respectively. The origin of this interesting distortion may presumably be found in the nature of the singly occupied orbital, which, by analogy with $CpMn(CO)_3$, is probably of $d_{x^2-y^2}$ or d_{xy} character and hence lies largely between the CO and PPh_3 ligands.[20] It would seem that the electron "hole" is localized largely between the carbonyl ligands, thus allowing closing of the OC–Mn–CO bond angle in response to the steric demands of the triphenylphosphine.[21] The metal–ligand distances of IV are all significantly longer than those of V, presumably because of a larger covalent radius for Cr(I) than for Mn(I).

Acknowledgment. Financial assistance from the Natural Sciences and Engineering Research Council, in the form of operating grants to S.F. and M.C.B., made this research possible.

Registry No. I, 36495-37-1; II, 12194-12-6; IV, 105121-81-1; $CpCr(CO)_3SnBu_3$, 105121-77-5; $[CpCr(CO)_3(THF)]I$, 105121-78-6; $[CpCr(CO)_3(THF)]Cl$, 105121-79-7; $[CpCr(CO)_3(THF)]Br$, 105121-80-0; $CpCr(CO)_3Me$, 41311-89-1; $CpCr(CO)_2(PPh_3)H$, 105121-82-2.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters for IV (6 pages); a listing of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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[13] The title compound crystallizes from 1:1 hexanes–ethyl ether in space group $P\bar{1}$ with a = 10.690 (6) Å, b = 11.543 (4) Å, c = 9.449 (5) Å, α = 103.94 (4)°, β = 101.46 (4)°, γ = 74.94 (4)°, V = 1081.20 Å^3, Z = 2, D_{calcd} = 1.337 g cm^{-3}, and μ = 6.051 cm^{-1}. An orange-brown crystal, 0.50 × 0.27 × 0.12 mm, was chosen for the collection of intensity data on an Enraf-Nonius CAD-4 diffractometer. The unit-cell parameters were obtained by a least-squares analysis of 25 centered reflections in the range $20 \leq 2\theta \leq 29°$. The data were collected by the θ–2θ scan technique, with variable scanning rate, using monochromated Mo radiation. A total of 3004 unique reflections were measured in the range $1 \leq 2\theta \leq 46°$, of which 2118 were considered observed, i.e., $I > 3\sigma(I)$. Three standard reflections were measured every 7200 s of radiation time and showed no significant variation during the course of data collection. The intensities were corrected for Lorentz and polarization effects. A numerical absorption correction was applied to the data: the transmission factors varied between 0.87 and 0.94.

The structure was solved by direct methods using the program MULTAN80.[14] Difference Fourier map calculations revealed the positions of all the hydrogen atoms. These were assigned temperature factors equal in magnitude to the equivalent isotropic values of their parent atoms and were included in the calculations, but not refined. Full-matrix least-squares refinement minimizing the function $\sum w||F_o| - |F_c||^2$, where $w = 4F^2/[\sigma^2(F^2) + (0.04F^2)^2]$ resulted in R = 0.038 and R_w = 0.050. The esd of an observation of unit weight was 1.898, the maximum shift to error ratio was 0.00, and the final difference Fourier synthesis was essentially featureless. The scattering factors used were those of Cromer and Waber,[15] and the anomalous dispersion coefficients were taken from Cromer.[16] All calculations were performed on a PDP 11/23 computer using the structure determination package of Enraf-Nonius, SDP.[17] The program ORTEP[18] was used for the preparation of the illustrations.

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[21] Presumably no such distortion would occur if the "hole" were in the alternative[20] d_{z^2} orbital.

Diphenyldiazomethane as a Six-Electron μ_4-Ligand in Metal Cluster Chemistry: Structural Characterization of $Ru_5(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C{\equiv}CR)(\mu_4\text{-}N_2CPh_2)(\mu\text{-}PPh_2)$ (R = Ph) and the Product of CO Insertion into the Nitrogen–Nitrogen Bond $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}C_2R)(\mu_4\text{-}NC(O)NCPh_2)(\mu\text{-}PPh_2)$ (R = *i*-Pr)

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Received July 23, 1986

Summary: Reaction of $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}C{\equiv}CR)(\mu\text{-}PPh_2)$ (R = Ph, *i*-Pr) with diphenyldiazomethane (Ph_2CN_2) afforded $Ru_5(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C{\equiv}CR)(\mu_4\text{-}N_2CPh_2)(\mu\text{-}PPh_2)$, the phenyl derivative of which has been shown by X-ray crystallography to contain an intact, μ_4-coordinated N_2CPh_2; these compounds are converted, in good yield, under CO to $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}C{\equiv}CR)(\mu_4\text{-}NC(O)NCPh_2)(\mu\text{-}PPh_2)$ via CO insertion into the N–N bond.

Diazo compounds are extensively used in organometallic chemistry as precursors of alkylidene ligands or as one-carbon fragments for carbon–carbon bond synthesis.[1,2] In addition an extensive coordination chemistry of intact diazoalkane molecules is known and a variety of terminal, η- and μ-bonding modes have been identified.[3-5] The propensity of metal clusters to bind unsaturated ligands in multisite fashion and the unsaturation implicit in the nitrene canonical form 1 of diazoalkanes might suggest additional modes of interaction in polynuclear systems. We describe herein the trapping of an intact diphenyldiazomethane molecule as a μ_4 six-electron ligand in the pentanuclear ruthenium cluster $Ru_5(CO)_{12}(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu_4\text{-}N_2CPh_2)(\mu\text{-}PPh_2)$ (2) and the insertion of CO into the N–N multiple bond of 2 to give a μ_4-acylnitrene cluster $Ru_5(CO)_{13}(\mu_4\text{-}\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)(\mu_4\text{-}Ph_2CNC(O)N)$ (3) as illustrated in Scheme I.

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