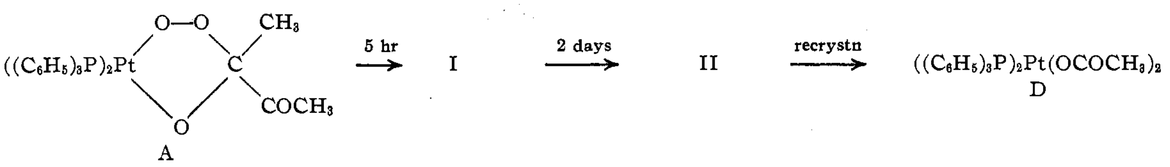

	A	I	II	D
Ir C=O	1710 vs	1825 m 1620, 1600 vs	1715 vs 1620, 1600 vs	1625 vs
Nmr Alkyl ^{1}H	2.29 (3) 1.43 (3)	2.19 (3) 1.32 (3)	2.07 (3) 1.32 (3)	1.37 (b)

2,4-dinitrophenylhydrazine derivative of $((C_6H_5)_3P)_2$-$PtO_2 \cdot C_2H_5COCOCH_3$ and the dinuclear adducts are quite stable.

Experimental Section

Materials.—The diketones, with the exception of *p*-methoxy-1-phenyl-1,2-propanedione were Eastman Organic Chemicals. The latter was prepared by oxidation of anisylacetone (ROC/RIC Co., Sun Valley, Calif.) with selenium dioxide using an adaptation of the method of Riley and Gray.[5] The required product was distilled under reduced pressure at 77° and was recovered as bright yellow-green crystals, mp 42–44°. The purity of all the diketones was checked by nmr, and in most cases, no further purification was considered necessary. The complex $((C_6H_5)_3P)_2PtO_2$ was prepared as previously described.[2]

Preparation of the Complexes.—Monoadducts were prepared as previously described.[2] The dinuclear compounds were prepared by warming gently, under an atmosphere of nitrogen, a 1:1 mixture of the mononuclear adduct and $((C_6H_5)_3P)_2PtO_2$ in the minimum of CH_2Cl_2 until the orange color of the solution faded to a pale yellow (*ca.* 5 min). Ether was added to precipitate the complexes, the purity of which could readily be checked by the disappearance of the ir bands due to starting materials at 820 and 1700 cm^{-1}. Excessive or prolonged heating caused decomposition of the complexes.

Dicarboxylates formed on allowing the mononuclear adducts to stand for periods varying between a few hours and several days (see discussion in text) in CH_2Cl_2 solution. Some unidentified dark organic material also formed but this could be minimized if the solution was kept under an inert atmosphere (N_2 or Ar). The 2,4-dinitrophenylhydrazine derivative of $((C_6H_5)_3P)_2PtO_2 \cdot C_2H_5COCOCH_3$ was prepared by adding, dropwise, a hot saturated ethanolic solution of the reagent to a solution of the complex in the minimum CH_2Cl_2. The orange derivative precipitated almost immediately, was filtered off, washed with ether, and dried *in vacuo*. See Table II for analytical results.

Physical Measurements.—Proton nmr spectra were obtained on a Varian A-60 spectrometer and the ir spectra on a Perkin-Elmer 700 (correct to ±5 cm^{-1}).

Table II
Analytical Results

Compound	Mp, °C	% C Calcd	% C Found	% H Calcd	% H Found	% P Calcd	% P Found
$R_1 = CH_3, R_2 = CH_3$							
Adduct A	106–108 dec	57.3	57.3	4.3	4.3	7.4	7.1
Dinucl adduct C[a]	111–115 dec	57.4	56.9	4.2	4.0	7.8	7.5
Carboxylate D	203–205	57.3	56.9	4.3	4.4	7.4	6.9
$R_1 = C_2H_5, R_2 = CH_3$							
Adducts A and B	138–140 dec	57.8	57.5	4.5	4.6	7.2	7.0
Carboxylate D	205–210	57.8	57.3	4.5	4.4	7.2	7.2
2,4-DNPH deriv of A and B[b]	275 dec	54.7	54.1	4.1	3.9	6.0	6.0
$R_1 = C_6H_5, R_2 = CH_3$							
Adducts A and B	105–108 dec	60.0	59.7	4.3	4.4	6.9	7.1
Carboxylate D	175 dec	60.0	59.7	4.3	4.3	6.9	7.0
$R_1 = p\text{-}CH_3OC_6H_4, R_2 = CH_3$							
Adducts A and B	110–125 dec	59.4	58.9	4.3	4.4	6.7	6.4
Carboxylate D	145–150 dec	59.4	58.6	4.3	4.0	6.7	6.1
$R_1 = C_6H_5, R_2 = C_6H_5$							
Adduct A	108–112 dec	62.4	61.3	4.2	4.2	6.4	6.0
Dinucl adduct C		60.3	58.9	4.1	3.9	7.2	6.2
Carboxylate D	206–208	62.4	61.6	4.2	4.1	6.4	6.1
$R_1 = CH_3COCH_2CH_2, R_2 = CH_3$							
Adduct A	131–133 dec	58.3	58.4	4.6	4.5	7.2	7.3
Dinucl adduct C[c]	122–126 dec	57.9	57.6	4.4	4.1	7.6	7.5

[a] Molecular weight: calcd, 1589; found, 1387. [b] Nitrogen analysis: calcd, 5.4; found, 5.2. [c] Molecular weight: calcd, 1617; found, 1035. There is considerable dissociation in solution.

Acknowledgment.—The authors wish to thank Dr. R. A. Bartsch for helpful discussions.

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Contribution from the Venable Chemical Laboratory,
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The Electron-Impact Ionization Potentials of Successively Substituted Acetylacetonates of Rhodium(III)

By Maurice M. Bursey*[1] and Peter F. Rogerson[2]

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We have continued our examination of ionization potentials measured with a mass spectrometer for series of metal acetylacetonates where each ring has a dif-

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[1] Research Fellow of the Alfred P. Sloan Foundation, 1969–1971.

[2] NSF Trainee, 1966–1970.

ferent local ionization potential.[3,4] These complement others' wide-ranging studies of chelate complexes where all the ligands are the same in a given complex.[5,6]

If ionization is efficient from the highest filled orbital, Hückel theory[7] with parameters set for agreement with visible spectra predicts a series of ionization potentials for the first transition series which are not observed even qualitatively;[6] on the other hand, the calculation is crude and may be of little predictive value.[8] At any rate, it calls for ionization from a metal-dominated orbital, and its failure has prompted much discussion about the possibility of ionization from a ligand orbital.

Our interest in the rhodium(III) complexes arose from two considerations: first, no data were available to compare magnitudes of trends in the first and second transition series; second, the electronic transitions observed for rhodium acetylacetonate complexes are qualitatively different from those observed for members of the first transition series. The low-energy bands in the spectra of the successively substituted chromium and cobalt complexes Ia–IVa and Ib–IVb have been

$M(acac)_3$
I
$M(acac)_2(3\text{-}NO_2acac)$
II
$M(acac)(3\text{-}NOacac)_2$
III
$M(3\text{-}NO_2acac)_3$
IV

a, M = Cr
b, M = Co
c, M = Rh

assigned[9] to the usual d–d transitions; these are not present in the rhodium series Ic–IVc, where the lowest energy transition corresponds to the $\pi-\pi^*$ transition of the ligand[9] near 315 nm in the spectrum of each compound. The possibility therefore existed that ionization from the ligand and the metal might play different roles in this series of compounds because of the significantly altered ordering of levels near the highest occupied molecular orbital. The alteration is seen not only in absorption results but in luminescence: while luminescence of Cr(III) chelates has generally been classified as metal-dominated d–d transitions,[10–12] the luminescence of rhodium acetylacetonate has been classified as ligand dominated ($\pi-\pi^*$ triplet to singlet).[13] The luminescence results are not directly applicable but serve merely to illustrate further aspects of the altered reactivity of rhodium.

If ionization occurs from the highest filled orbital on any of the ligands, the simple picture assuming independence of the orbitals of each ligand would require that as long as any ring in compounds I–III remains unsubstituted, the electron should come from that orbital; hence, for ionization from the ligand, these compounds should come from that orbital; hence, for ionization from the ligand, these compounds should have nearly the same ionization potential while that of IV should be considerably higher. Ionization from a metal-dominated orbital or any orbital in which each ligand influences the orbital energy equally should give a steady progression of ionization potentials. Reference to Figure 1 indicates that this second picture fits the experiment and in comparison with the data for Cr(III)[4] shows that there is no qualitative change in the susceptibility of ionization potentials to substitution on going from Cr[14] to Rh, in spite of the altered order of energy levels. Once again, adherence to one or the other of these simple pictures requires that ionization come from the metal. More complex models can be envisioned in which ionization from the ligand is compatible with the observed results, however.

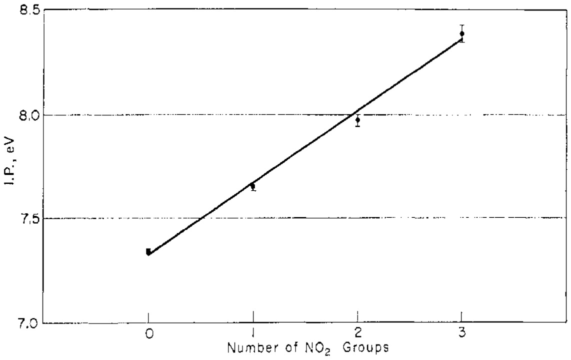

Figure 1.—Linear progression of ionization potentials on successive introduction of 3-nitro substituents in tris(acetylacetonato)rhodium(III). Values determined for various compounds: Ic, 7.34 ± 0.01 eV; IIc, 7.65 ± 0.02 eV; IIIc, 7.97 ± 0.03 eV; IVc, 8.39 ± 0.04 eV. The quoted errors are standard deviations of data obtained in triplicate on each of 2 different days (total determinations, six) and do not represent estimates of accuracy.

One of these requires that energy be transmitted very inefficiently through the central metal atom and that ionization occur from the ring first interacting with the ionizing electron. The ion current would then be a composite of the appropriate ion current from ionized unsubstituted and the appropriate ion current from ionized substituted rings, which should be additive under the conditions of low transmittal of energy. The ionization efficiency curve for a compound with mixed chelate rings such as II or III would then be expected to fall between the curves for the completely substituted and the completely unsubstituted compounds, the spacing being determined by weighting of the contributions from each type of ring. On the other hand, there would be breaks in the ionization efficiency curves if this is the case; Figure 2 shows that no breaks are observed. They may be masked by the convolution of the ionization efficiency with the thermal electron

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(5) (a) G. M. Bancroft, C. Reichert, and J. B. Westmore, *ibid.*, **7**, 870 (1968); (b) G. M. Bancroft, C. Reichert, J. B. Westmore, and H. D. Gesser, *ibid.*, **8**, 474 (1969); (c) C. Reichert and J. B. Westmore, *ibid.*, **8**, 1012 (1969); (d) C. Reichert, G. M. Bancroft, and J. B. Westmore, *Can. J. Chem.*, **48**, 1362 (1970).

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(14) Or Co, for which the ionization potentials of the successively substituted compounds Ib–IVb are also equally spaced. The low intensities of the molecular ions of IIIb and IVb make assignment of absolute values to the IP's difficult, though they appear to be in the same range as the other series.

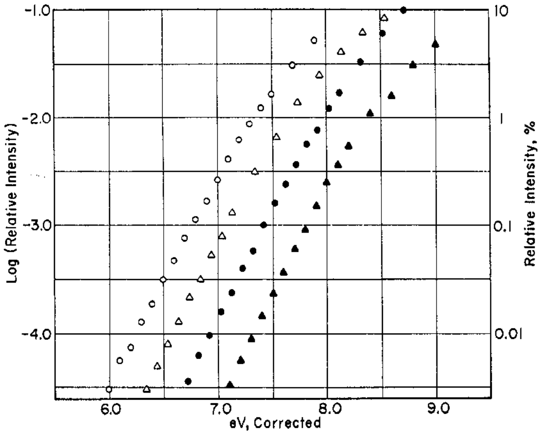

Figure 2.—Ionization efficiency curves representative of data from which the values plotted in Figure 1 were taken at the 1% level; the curves, left to right, are for compounds Ic, IIc, IIIc, and IVc.

energy spread.[15-17] There is evidence that for some mechanisms of intersystem crossing (but not all) energy transmission to the metal in the rhodium complex Ic is an inefficient process as the weak influence of spin-orbit coupling on triplet-state lifetimes indicates.[13] Otherwise there is little precedent for this model, since ionization usually occurs from the orbital of highest energy in the entire molecule.[18]

Alternatively, the possibility exists that substitution in one ring influences the ionization potential of the whole system so greatly that it is improper to speak of localization on an individual ring. Again in organic systems, π systems of the same molecule, perpendicular to each other but in close proximity, influence each other's energy manifolds dramatically.[19]

Finally, the magnitude of the shift of the IP (1.05 ± 0.05 eV for three groups) on nitration of the Rh(III) complex differs from the magnitude of the same shift for the Cr(III) complex (0.75 ± 0.08 eV). This difference is real, as a review of our error analysis shows. Interior points fall close to the line in these examples; the usual deviation from anticipated linear correlations[20] produced by our method is on the order of 0.02–0.03 eV. Consequently, there is a distinct difference between the susceptibility of the ionization potential to the substituent in the Cr(III) series and in the Rh(III) series. This fact is difficult to reconcile with the picture in which ionization occurs entirely from the ligand in both systems and indicates that some other picture—possibly one of those we have noted above for both systems or different models for each system—must be maintained.

Acknowledgment.—We thank Professor J. P. Collman, Stanford University, for a gift of the compounds used in this study; the technique of measuring IP's is an adaptation of the energy compensation technique[21,22] which we have already described.[4,23] We gratefully acknowledge support of this work by the National Science Foundation (GP 8096) and by the University Research Council of the University of North Carolina.

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[15] Even at 4.5 orders of magnitude below the normal intensity of the molecular ion we do not detect breaks in the curve which might be expected if inefficient (1%) ionization processes existed from other orbitals besides the one which produces ions efficiently, a model suggested by photoelectron spectroscopy studies.[16] We note that present-day photoelectron spectroscopy does not include mass analysis.[17]

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Mössbauer Spectroscopy of Tin(IV) Oxyhalides

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Of the numerous parameters which can be extracted from ^{119}Sn Mössbauer spectra, the isomer shift (IS) and quadrupole splitting (QS) have been of greatest interest to the chemist.[2] In relating the IS of tetrahedral tin-halogen compounds, SnX_4, to other parameters which describe the bonding interaction between the metal atom and its ligands, it was noted[3] that for X = Cl, Br, or I, there is a linear relationship between the ligand electronegativity and the IS extracted from the Mössbauer spectrum. Such an IS-electronegativity correlation has recently been extended to octahedral SnX_6^{2-} complexes,[4,5] making use of Mulliken electronegativities. For both the tetrahedral and octahedral compounds it is observed that the isomer shift decreases as the electronegativity increases (Figure 1). From the relationship between the IS parameter and the electronic wave functions for the s electrons surrounding the ^{119}Sn nucleus it is by now well established[6] that a decrease in the isomer shift implies a decrease in the 5s electron density at the nucleus assuming that all measurements either are made using the same ^{119}Sn source or (preferably) are referred to a standard absorber.[7]

A similar linear correlation for trimethyltin halides is also observed, despite the fact that there are significant structural differences between $(CH_3)_3SnF$ (which is a nearly trigonal-bipyramidal polymer[8]) and $(CH_3)_3SnI$ (which can be described as having a distorted tetrahedral structure). It should be noted, however, that the slope $d(IS)/d\chi$ for these compounds is very much

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[1] Fullbright-Hayes Scholar, 1968–1969.

[2] For a general review of this field, see V. I. Gol'danskii and R. H. Herber, Ed., "Chemical Applications of Mössbauer Spectroscopy," Academic Press, New York, N. Y., 1968.

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